Discovery and characterization of contrasting siderophores produced by related nitrogen fixing bacteria using high resolution LC-MS

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Azotobacter vinelandii (AV) and Azotobacter chroococcum (AC) are closely related N₂ fixing bacteria. Whereas the structures and physiological functions of siderophores produced by AV have been much studied, those of AC remain unidentified beyond a general chemical characterization. Here we have exploited the characteristic iron isotopic fingerprint to identify known and unknown siderophores and characterize them structurally using ultra-sensitive high-resolution nano-flow UPLC-MS on an LTQ-Orbitrap XL platform.

Interrogation of preliminary data for AV revealed many putative Fe-chelators with high abundances, including those previously identified and other, yet unreported compounds. Siderophores produced by AC were unrelated to those of AV. Many AC siderophores possess aliphatic side chains of variable length with corresponding changes in hydrophobicity. Current work investigates how these chemical differences in siderophore production relate to different metal acquisition strategies and occupation of different ecological niches.

Using isotopic analysis of copper to assess copper transport and partitioning in wetland systems

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Copper isotopes (δ⁶⁵Cu/δ⁶³Cu) are potentially powerful new geochemical proxies for transport and oxidation–reduction processes in hydromorphic soils, rivers and lake sediments. However, the integrative signal of δ⁶⁵Cu has not been used so far to investigate the transport and partitioning of copper in wetland systems with respect to both hydrological and biogeochemical conditions. Here we used copper isotopes to investigate the copper cycling in a stormwater wetland (as a ‘natural laboratory’) that regularly received copper-contaminated runoff from a 42 ha vineyard catchment (Rouffach, Alsace, France). Runoff water, suspended solids, sediments and plants were regularly collected throughout the period of copper-based fungicides application (May to July 2011) to establish the copper mass balance and study isotopic fractionations.

60 to 93% of copper in runoff was associated with suspended solids, which were efficiently retained by the wetland (93 to 96%). Copper bound to suspended solids had negative isotope signatures (-0.33 to -0.1 ± 0.1‰), whereas dissolved copper was enriched in δ⁶⁵Cu (0.23 to 1.35 ± 0.06‰). Dissolved copper retention largely varied (68 to 95%) and became depleted in δ⁶⁵Cu when passing through the wetland (δ⁶⁵Cu_inlet-δ⁶⁵Cu_outlet: 0.03 to 0.77 ± 0.08‰). This isotopic shift suggests that copper rapidly sorbed to organic matter or mineral phases of the wetland sediments. Under high-flow conditions, copper was less retained by the wetland and was likely mobilised from the wetland sediments. This was attested by a lower δ⁶⁵Cu value of the outflowing dissolved copper, thereby reflecting the contribution of sediment-bound copper (0.02 ± 0.1‰). Copper uptake by the vegetation (Phragmites australis, Cav.) was not a significant retention process in the wetland, and accounted for less than 1.5% of the total copper amount in the wetland.

We anticipate our results to be a starting point for using copper isotopes in a comprehensive approach to evaluate processes affecting copper cycling in hydro-biogeochemically dynamic systems, such as wetlands or hyporheic zones.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
High-precision Nd isotope and HFSE analysis of Deccan Traps weathering profiles

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Accurately quantifying the flux of elements from landmasses during pedogenesis necessitates knowledge of the parent rock chemistry and some control on whether allochthonous materials (e.g., dust) have been added to the profile during exposure. This is important, for instance, in calculating weathering rates from U-series isotopes in young profiles or interpreting stable isotope depth signatures. The Deccan Traps provide an ideal natural laboratory for studying chemical weathering due to the thick succession of mafic flows which have been weathered to varying degrees on different time scales. In addition, the isotopic and elemental composition of the basalt parent rock contrasts significantly with most potential dust sources (e.g., Archean-Proterozoic crust of the Dravidian Shield).

Deeply weathered laterite of the Deccan Traps has experienced significant accumulation of aeolian material during its long exposure history. For example, in a full laterite profile near Bidar, an upward increase in Th concentration and accompanying decrease in the Nb/Th ratio is evident from the profile near Bidar, an upward increase in Th concentration and accompanying decrease in the Nb/Th ratio is evident from the base to top. If Nb is assumed to be immobile during its long exposure history. This “blind dating” procedure has been questioned before but it is still commonly used. Here we present a case study on carbonates from the basalt units of the Bambuí Group (central Brazil) where Sr, C, and O isotope ratios are well correlated with the 13C negative values and was dated at 740 ±22 Ma, indicating a Sturtian age. Limestones and dolostones of carbonate rocks have been extensively sampled across two identifiable basalt flows. The Deccan Traps provide an ideal natural laboratory for studying chemical weathering due to the thick succession of mafic flows which have been weathered to varying degrees on different time scales. In addition, the isotopic and elemental composition of the basalt parent rock contrasts significantly with most potential dust sources (e.g., Archean-Proterozoic crust of the Dravidian Shield).

Near Chhindwara, a sub-Recent weathering profile is exposed which spans across two identifiable basalt flows. The individual flows can be fingerprinted with variations in their HFSE composition, highlighting another important consideration in mass balance calculations of a weathering profile. Even more interesting, however, are the uppermost samples of the lower exposed flow with alkali element, HFSE ratios, and subtly less radiogenic Nd isotope values which again suggest contamination with an allochthonous component. This is interpreted to represent the entrainment of sediment in the lava flow top during emplacement or the accumulation of dust during post-eruption volcanic quiescence prior to the emplacement of the overlying flow.

U-Pb dating vs. Sr isotope chem stratigraphy on Neoproterozoic carbonates: Shedding light on blind dating?

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Sr isotope ratios of carbonate rocks have been extensively used for global correlations especially on Precambrian rocks due to lack of fossils and scarcity of dating targets to constrain their depositional ages. This “blind dating” procedure has been questioned before but it is still commonly used. Here we present a case study on carbonates from the basal units of the Bambuí Group (central Brazil) where Sr, C, and O isotope ratios are well correlated with the 13C negative values and was dated at 740 ±22 Ma, indicating a Sturtian age. Limestones and dolostones of the Bambuí Group are organic-rich limestones displaying highly positive δ13C values. All carbonates, including those overlying the diamictite, show δ13C values close to the Precambrian-Cambrian boundary or even younger, when more radiogenic Sr isotopes ratios (ca. 0.7085) are expected. This may result from a restricted sea context for the Bambuí carbonate platform; consequently their Sr isotope ratios do not correspond to that of contemporaneous oceans. Several lines of evidence suggest this is not an unusual scenario for Neoproterozoic carbonate platforms. Our work shows that worldwide correlations based only on Sr isotopes must be considered with caution.
Rocky constraints on catabolic energy supply in the subseafloor

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Reactions between circulating seawater and oceanic basement release reduced components, which can be used as electron donors by chemolithoautotrophs in the subseafloor. High-temperature axial hydrothermal vent systems show a pronounced influence of basement composition on metabolic diversity, with ultramafic hosted systems supporting a greater range of catabolic reactions, including anaerobic ones [1].

We investigate the influence of temperature (2-110°C), rock composition (basalt vs. peridotite), and permeability on energy availability for a subseafloor biosphere away from axial vents where seawater circulation through fractured basement takes place at lower temperatures.

In fresh basalt, oxidation of ferrous iron is the main energy source at low temperatures (<25°C) and under oxic conditions. Increasing extents of alteration of glassy lava will build up palagonite rims as diffusive barriers between the fractures and unaltered glass, which slow down the rates of alteration. Palagonite has little or no ferrous iron and is enriched in U and K. Unless new fractures form and allow circulating seawater to interact with fresh material, the principal source of energy will change to dihydrogen produced radiolytically by U and K.

At moderate temperatures (25-60°C), recharge of oxygenated seawater is sluggish and anaerobic metabolic reactions become more important. At high temperatures (60-110°C), the metabolic energy demand has increased relative to the energy supply, making growth more difficult for microbes.

In mantle peridotite, abundantly exposed in rift mountains along slow spreading ridges and commonly strongly serpentinitized, oxidation of ferrous iron is also the main energy source at T<25°C. Brucite dissolves in contact with cold seawater, increasing permeability of the rock and pH in the interacting fluid. Serpentinites are often pervasively affected by low-T reactions, indicating that new permeability develops in the course of interaction with seawater. At T>25°C, dihydrogen yields are very high throughout. While the increased energy supply and permeability will facilitate microbial growth, high pH and the dearth of CO₂ in the interstitial solutions may impede it.


Contaminant geochemistry and migration in three different mine sites in Finland – Comparison of anthropogenic and geogenic contamination for risk assessment

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Areas with bedrock abundant in ore minerals have naturally high amount of harmful elements in soil as well as in ground and surface waters. After the beginning of the mining the anthropogenic contamination also tends to increase. Thus, it is important to estimate the effects of mining activity and water treatment methods to the geogenic background when assessing the long term effects to the surrounding environment. In this study, geochemical and anthropogenic contaminant geochemistry and transport in soil at three different mine sites in Finland: Suurikuusikko, Siilinjärvi and Luikonlahti, were characterized by using extraction methods and mineralogical studies. Water samples were analyzed for metal and metalloid concentrations, anions and physico-chemical properties. Also groundwater and geochemical modeling software were used to study the groundwater flow paths and hydrogeochemistry.

The results show that the geogenic background, the hydrogeology of the site and concentrations of harmful elements in mine wastes and waters must be considered in risk assessment of mine sites. When evaluating the risks, the concentration levels must be compared to geochemical background, but also the ratio of available, potentially mobile and total concentrations must be studied, because the mining activities tend to increase the proportion of potentially mobile and available elements. Due to residues of chemicals used in enrichment process and weathering of minerals during the process, the concentration profile of harmful elements in waters can be used to distinguish the anthropogenic and geogenic contamination. Results also indicate that fractures of crystalline bedrock are important pathways for contaminant migration to environment and should be studied using geophysical methods and groundwater flow modeling when assessing the environmental effects of mines.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Surface complexation on birnessite controls Pb distribution in heavily contaminated soil and karst groundwater

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At the historic mineries of Priddy near Bristol, soils are heavily contaminated with up to 2000 mg/kg Pb. However, porewater concentrations of Pb are undersaturated with respect to natural common Pb minerals such as cerussite. Scanning electron microscopy and EDX analysis revealed that the Pb in Priddy soil is associated with a poorly-crystalline Mn oxide phase. The Mn oxide phase contains up to 40 wt. % Pb. Using µ-EXAFS spectroscopy, and µ-XRD, we identified the Mn oxide as birnessite, similar to the poorly crystalline microbial δ-MnO2 described by Villalobos et al. [1]. However, the origin of the birnessite in Priddy soil is unclear. Using µ-EXAFS, we find that Pb is complexed on both edge and vacancy sites, as proposed by [2].

The hydrology of the mining area drains into a complex network of caves, with the resurgence at Wookey Hole. Within the caves are extensive coatings of birnessite (as identified using XRD and Raman spectroscopy). We hypothesise that this birnessite is of microbial origin as found elsewhere [3]. The soil birnessite must be reduced to release dissolved Mn(II) which is then oxidized in the dark cave system by chemolithoautrophic bacteria. The secondary birnessite in the cave also contains up to 40 wt. % Pb. µ-EXAFS shows that Pb associated with this birnessite in both edge and vacancy surface complexes.

We hypothesise that the complexation of Pb by birnessite controls the dissolved Pb concentration in soil pore water and groundwater. To test this, we have performed a series of batch sorption edge experiments with synthetic birnessite and fit these to derive equilibrium expressions and constants for the possible surface complexation reactions. Using our surface complexation model, we are predicting the concentration of Pb in soil porewater and groundwater. However, a reactive transport model needs to account for the microbial birnessite recycling.

References:

U-Pb and Hf isotope characteristics of zircon from chromitites at Finero

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The Finero phlogopite-peridotite represents a metasomatized residual mantle harzburgite, exposed at the base of the lower-crust section in the Ivrea Zone, Western Alps [1]. Previous studies point to one or more Late Paleozoic mantle metasomatic events in the Finero peridotite, although there is little agreement regarding the relative timing of different events or the source of the metasomatising agents.

Studied chromitite samples derived from the dump in the prospecting trenches of Alpe Polunia and Rio Creves. Dominant zircon population is pale pink and show different shapes (subhedral, subrounded or elongated). In cathodoluminescense (CL), the main set of population is represented by complex grains, which show development of core-rim relationship (most likely recrystallized rim on a preserved core). Subordinate zircon grains are colourless, with a smoky cathodoluminescense and almost no internal pattern.

Three main U-Pb age clusters have been identified. The youngest cluster, typical for subordinate zircon population and rims in complex grains from dominant population, yielded two 206Pb/238U ages (e.g., 208.6 ± 4.0 Ma, MSWD=2.0, n=8 and 194.9 ± 3.4 Ma, MSWD=0.45, n=3, respectively). The other clusters represent cores and rims in the composite grains, with ages 288.3 ± 7.3 Ma (MSWD=3.3, n=6) and 248.6 ± 3.3 Ma (MSWD=0.13, n=8), respectively. In Lu-Hf systematics, zircons of all age populations show a relative narrow spread in 176Hf/177Hf(t) values, with majority (~90 %) falling between 0.282652 and 0.282533. An increase in 176Hf/177Hf(t) ratio from old to young zircon populations defines a trend, which follow CHUR evolution curve.

Our data do not concur with the assumption [2] of a single metasomatic event during chromitite formation. In contrast, a prolonged formation and multistage evolution of zircon growth is considered a feature typical of a metasomatized subcontinental mantle at Finero.

This investigation was supported by the Uralian Branch of Russian Academy of Sciences (grant 12-P-5-1020).

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DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
The effect of 1,10-phenanthroline on the oxidative dissolution of iron monosulfide (FeS)

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The effect of 1,10-phenanthroline (a Fe²⁺ ligand) on the oxidative dissolution of synthetic iron monosulfide (FeS) was tested by using electrochemical methods. The experiments were performed in air-saturated HCl solutions with the concentration of 1,10-phenanthroline in range 0-1 mM, at pH 5 and 25°C. The corrosion current densities (i_{corr}), corrosion potentials (E_{corr}) and values of the components of equivalent circuit that fits the Electrochemical Impedance Spectroscopy (EIS) data were determined.

i_{corr} values are quasi-constant when the concentration of 1,10-phenanthroline varies between 0 and 0.5 mM. When the concentration of 10-phenanthroline exceeds the value of 0.5 mM, i_{corr} increases from 30.7 µA cm⁻² up to 38 µA cm⁻². E_{corr} increases from -393 mV up to -338 mV when the concentration of 1,10-phenanthroline increases from 0 to 0.5 mM. At higher concentrations of ligand, E_{corr} decreases down to -355 mV. The values of the components of equivalent circuit that fits EIS data were found to be in agreement with the variation of i_{corr} and E_{corr}.

Our conclusion is that the oxidative dissolution of FeS in the presence of 1,10-phenanthroline is the result of two processes with opposite effect: 1) the inhibiting adsorption of 1,10-phenanthroline on the FeS surface and 2) the promoting effect of 1,10-phenanthroline on the breakage of Fe-S bond.

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI–UEFISCDI, project number 51/2012.

Earth’s building blocks: The “Core Spyglass”

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The details of Earth’s accretion, and the nature of Earth’s building blocks in particular, are still poorly understood. One way to constrain accretionary processes is to understand the major differentiation event that took place during accretion: core formation. Earth’s core formed during accretion as a result of melting, phase-separation, and segregation of accretionary building blocks (meteorites, planetesimals, protoplanets). Extensive melting lead to the formation of a Magma Ocean, and the bulk compositions of the core and mantle depend on it evolution (pressure, temperature, composition) during accretion. The entire process left a compositional imprint on both reservoirs: in the silicate Earth, in terms of siderophile trace-element concentrations (a record that is observed in present-day mantle rocks); and on the core, in terms of major element composition and light elements dissolved in the metal (a record that is observed by seismology through the core density-deficit).

Constraining accretionary processes by looking at the core has been studied for almost ten years. Based on partitioning of slightly siderophile elements, the current paradigm is that Earth must have formed under very reducing conditions, followed by a complex oxidation mechanism to reach the present-day redox state. In the light of new partitioning data under extreme conditions, we will show here that Earth can form at a constant redox state (the present-day value), or even form in relatively oxidized conditions (that of carbonaceous or ordinary chondrites). This paradigm shift is strengthened by the fact that oxidizing conditions favour oxygen solubility in the core, which is a requirement both for the inner-core density jump and outer core density deficit.
Advances in instrumentation based on cavity enhanced laser absorption spectroscopy

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Novel instrumentation based on high-resolution laser absorption spectroscopy now allows high precision measurements of gas concentration and isotopic ratios continuously, in real time, and without preconcentration. These analyzers employ tunable lasers that operate in the near-infrared and mid-infrared spectral regions and employ an optical cavity as a measurement cell. The simple operation of these instruments allows measurements almost anywhere. The laser wavelength is continuously and repetitively scanned over selected absorption features of target isotopologues to record high-resolution absorption lineshapes at data rates of 1 Hz or faster. The integrated areas of the measured lineshapes enable determination of the respective isotope-specific concentrations directly. No longer constrained to operate in a laboratory, these analyzers offer opportunities to record measurements in remote sites in less-developed areas. This presentation will summarize recent developments at LGR in both hardware and software analysis that enable measurements of isotopic ratios in carbon dioxide (\(^{13}C, {^{18}}O, CO_2\)), methane (\(^{13}C, CH_4\)), nitrous oxide (\(^{15}N_2, {^{15}}N, {^{18}}O, N_2O\)) and water (liquid and vapor; \(^{2}H, {^{17}}O, {^{18}}O, H_2O\)) in ambient air and in complex gas samples. An overview of the current performance of LGR instruments and perspectives on future developments will be presented.

Ca isotope fractionation in a permafrost-dominated boreal ecosystem (Kulingdakan watershed, Central Siberia)

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Ca isotope compositions were measured in different compartments (stream water, soil solutions, rocks, soils and soil leachates and vegetation) of a small permafrost-dominated forested watershed in the Central Siberian Plateau. Our results show that only the processes related to vegetation activity significantly fractionate Ca isotopes within the watershed. These fractionations occur during Ca uptake by roots and along the transpiration stream within the larch trees. Biomass degradation then significantly influences the Ca isotopic compositions of soil solutions and soil leachates via the release of light Ca. Furthermore, organic and organo-mineral colloids originated from organic matter degradation are thought to affect the Ca isotopic composition of soil solutions by preferential scavenging of \(^{40}Ca\). This imprint of organic matter degradation on the \(^{44}/^{40}Ca\) of soil solutions is much more significant for the warmer south-facing slope of the watershed than for the shallow and cold soil active layer of the north-facing slope, indicating that the available stock of biomass and the decomposition rates are critical parameters that regulate the impact of vegetation on the soil-water system. Moreover, the obtained \(^{44}/^{40}Ca\) patterns contrast with those described for permafrost-free environments with a much lower \(^{44}/^{40}Ca\) fractionation factor between soils and plants, suggesting particular processes related either to the presence of permafrost or to the specific features of organic matter degradation in permafrost environments. Finally, biologically induced Ca fractionation observed at the soil profile scale is not visible in stream and river waters, whose isotopic variability in the course of the year is likely controlled by the lithological heterogeneity of the sources. As such, we suggest a negligible influence of biologically related fractionation on the long-term Ca isotopic signatures of riverine fluxes carried to the ocean.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Effect of Fe(II) ions on the sorption of selenite onto chlorite

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It has been reported that Fe(II)-bearing minerals or Fe(II) ions can reduce oxoanionic selenite (Se(IV)O₃²⁻) either to Se(0) or Se(-II) and then decrease the mobility of the selenite in subsurface environments [1, 2]. In this study the effect of Fe(II) ions on the sorption of selenite onto chlorite surfaces was investigated as a function of selenite concentration, Fe(II) concentration, and pH.

The sorption of Se(IV) onto chlorite surfaces followed the Langmuir isotherm regardless of the presence of Fe(II) ions. The Se(IV) sorption was enhanced at a pH > 6.5 when the Fe(II) concentration was higher than 5 ppm because of the increased sorption of Fe(II) onto chlorite surfaces. XANES (X-ray absorption near edge structure) spectra of the Se K-edge showed that most of the sorbed Se(IV) was reduced to Se(0) by Fe(II) sorbed on the chlorite surfaces, especially at pH > 9. The combined results of field emission scanning electron microscopy and X-ray diffraction also showed that elemental selenium and goethite were formed and precipitated on the chlorite surfaces during the sorption of selenite. Consequently it can be concluded that Se(IV) can be reduced to Se(0) in the presence of Fe(II) ions by the surface catalytic oxidation of Fe(II) into Fe(III) and formation of goethite at neutral and particularly alkaline conditions.

**Figure 1:** The sorption of Se(IV) onto chlorite surfaces as a function of pH at different concentrations of Fe(II) ions.

Horizontal gene transfer in phylogenetically-distant taxa that induce the formation of modern wrinkle structures: Implications for the interpretation of Earth’s earliest microbialites

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Wrinkle structures in rocks dating back to the Archean are commonly interpreted to represent the stabilizing influence of cyanobacteria on sediments because the trapping and binding of sediment by these phototrophic microbes is known to produce similar features in modern tidal flat settings [1]. Our observations of modern sediments show that, like cyanobacteria, chemolithotrophic taxa within the Beggiatoaceae can produce features that are reminiscent of those found in the ancient rock record. Despite similarities in cell morphology and division patterns, the Cyanobacteria and the Beggiatoaceae are generally considered to be phylogenetically-distant clades in rRNA-based phylogenies. However, our comparisons of Beggiatoa and cyanobacterial genomes show that these organisms share many genes that potentially code for phenotypic traits such as chemotaxis, filament formation, and the production of extracellular polymeric substances. Some of these genes may underlie the similar biostabilizing influences these organisms impart on sediments. Our analyses further suggest that at least some of these genes may have been acquired via horizontal gene transfer. The presence of multiple biostabilizing clades in the modern, as well as the potential for extensive horizontal gene transfer over 3.5 billion years of evolution, complicates the interpretation of ancient sedimentary features using solely morphological criteria.


Development of a novel TOF-SNMS to analyze sub-micron noble gas distribution

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Overview of the instrument

Ion beam for secondary ion mass spectrometry (SIMS) down to 10 nm can reveal new perspectives for cosmochemistry and material sciences. We have developed LIMAS (Laser Ionization Mass Nanoscope [1]) that is a time-of-flight sputtered neutral mass spectrometer (TOF-SNMS) with non-resonant laser post-ionization system. LIMAS is mainly composed of Ga focused ion beam (FIB) for sputtering, femtosecond laser for post-ionization of the sputtered particles, and high mass resolution multi-turn mass spectrometer of which mass resolving power of 4He+ (m/z ~ 4) is 8,500 (FWHM) after 90 cycles.

One of our goals is to determine micro-distribution of noble gases in solids derived from solar wind (SW) irradiation. An ultra-fine ion probe and post-ionization procedure should reveal the processes of the solar-gases were implanted and the surface layer was lost by space weathering irradiation. An ultra-fine ion probe and post-ionization procedure should reveal the processes of the solar-gases were implanted and the surface layer was lost by space weathering irradiation.

The performance of LIMAS should be improved towards higher sensitivity and lower background noises because bulk concentrations of solar-He in gas-rich meteorite are ~1016−1018 atoms/cm3 [2] for rocky material (density ~ 3 g/cm3).


The association between iron and carbon in freshwater colloids

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Iron and carbon are important constituents of natural colloids, which intimately links the fate of these two elements in riverine systems. Iron may strongly affect the binding of trace metals by organic matter, e.g., through competition for binding sites, which highlights the importance of a correct appreciation of the Fe speciation in surface waters. However, the chemistry of Fe and C in natural colloids is complex and depend on many factors including the pH, the Fe:C ratio, and the redox speciation of Fe [1-3].

Two areas with a contrasting Fe chemistry were studied: a lowland area with widespread seepage of iron-rich groundwater, and an upland peat area. Samples of tenoxic, well-mixed streams were subjected to cascade filtration using conventional filtration (1.2 µm, 0.45 µm, 0.1 µm) and cross-flow ultrafiltration (CFF; 5 kDa). The colloidal fraction, here operationally defined as between 0.45 µm and 5 kDa, was isolated by CFF and subsequently freeze-dried. The speciation of colloidal Fe was determined by EXAFS spectroscopy at the Fe K-edge (MAX-lab, Lund, Sweden).

In the rivers draining upland peatland, Fe and C were predominantly recovered in the fraction between 5 kDa and 0.1 µm. Conversely, in the rivers draining the lowland with extensive seepage of iron-rich groundwater, Fe was most abundant in the >0.1 µm fraction, whereas C was predominantly present < 0.1 µm. The EXAFS data reveal that colloidal Fe speciation is different in both study areas. It exists as mononuclear Fe complexed by dissolved organic matter, as colloidal hydrous ferric oxides (likely stabilized by adsorbed organic matter), or as a mixture of these. The colloidal Fe concentrations show considerable seasonal variability. Overall, this study contributes to a better understanding of colloidal Fe speciation and of its interaction with organic C.


DOI:10.1180/minmag.2013.077.5.2

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Asian Monsoon moisture transport 1999-2005 and its implications for palaeomonsoon reconstructions

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The Asian summer monsoons affect the livelihood of the world’s most populous regions. Predictions of future monsoonal variability require reliable palaeoclimate reconstructions from proxy data. Speleothem δ¹⁸O records from Chinese cave sites are assumed to provide direct palaeomonsoon intensity records, but recent research suggests δ¹⁸O integrates a more complex climate signal. We detected the sources modern monsoonal precipitation across China using a Lagrangian precipitation source diagnostic and reanalysis data. Our results show that monsoonal precipitation (May-August) in this region is primarily derived from the northern and western Indian Ocean; identification of this signal is consistent with recent GCM results. We also find that recycled moisture over continental Indo-China is an important contributor to west-to-east moisture transport during the monsoon season. These data highlight the importance of proxy site location and improve our ability to isolate the precipitation amount or monsoon intensity signal in palaeomonsoon reconstructions.

Trace element and ²⁶Al–²⁶Mg constraints on silicate differentiation of the HED parent body

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The howardite–eucrite–diogenite meteorites are considered to originate from the asteroid Vesta. Diogenite meteorites appear to be mafic cumulates with a pyroxene-dominated mineralogy, whereas eucrites are basaltic in mineralogy and composition. However, the relationship(s) between these products of silicate differentiation of their parent asteroid(s) remain enigmatic, if indeed they originated from the same parent body as is suggested by their common three-oxygen isotope compositions.

We have conducted a detailed in situ major and trace element study of minerals (pyroxene and plagioclase) in a large number of diogenites and non-cumulate eucrites (n = 44) by LA-ICPMS. We have also analysed to ultra-high precision (²⁶Mg* ± 0.002‰) the Mg isotopic composition of the same bulk meteorites by MC-ICPMS. Significant variations in ²⁶Mg* related to ²⁶Al decay in the first 5 Myr of the Solar System are evident amongst the suite of diogenites (²⁶Mg* = –0.011‰ to +0.013‰) and eucrites (²⁶Mg* = +0.004‰ to +0.0040‰). Despite their limited range in mineral major element compositions, mineral trace element concentrations vary widely. For example, moderately incompatible heavy rare earth element concentrations in pyroxene vary by more than two orders of magnitude (e.g., Yb = 0.02 to 3.1 ppm).

Trace elements such as Yb in pyroxene and Sr in plagioclase co-vary with bulk rock ²⁶Mg* values, which potentially implies rapid magmatic differentiation of a magma ocean. However, the large range of trace element abundances is difficult to reconcile with any simple cogenetic model for partial melting or crystallization of diogenites (cumulates) and eucrites (residual liquids) from a common parent body or magma ocean. Stable Mg isotopic compositions (²⁵Mg) of eucrites appear to be distinct from those of both diogenites and terrestrial basalts, which might imply that diogenites and eucrites originated from separate parent bodies or that eucrites are the product of a formation process (i.e., residual liquids of extensive fractionation of an ultramafic magma body) that is fundamentally different to the partial melting processes that produces basaltic magmas on Earth.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Environmental fate, transport, and bioavailability of CeO₂ nanoparticles in stream mesocosms

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Emissions from wastewater treatment facilities (“press”-type exposures) and accidental spills (“pulse”-type exposures) are two possible entry routes of engineered nanomaterials into aquatic environments. Significant uncertainty exists regarding the processes governing transport and environmental fate of these novel materials. Outdoor, 1870L recirculating stream mesocosms were treated with either 1) a one-time addition (pulse) of acetate-coated cerium dioxide nanoparticles (CeO₂ NPs) to achieve aqueous concentration of 10 mg NPs/L or 2) a 25-day continuous exposure (press) of the same amount of NPs, such that periphyton concentrations of Ce in the press-dosed stream averaged 1.2 mg/L on day 15 (12% of target) and 1.1 mg/L (11% of target dose) on day 25. Five days after completion of NP dosing in press mesocosms (day 30 of experiment), aqueous Ce concentrations had declined to an average of 0.02 mg/L by cessation of the experiment on day 30. Aqueous Ce concentrations in the press-dosed stream averaged 1.2 mg/L on day 15 (12% of target) and 1.1 mg/L (11% of target dose) on day 25. Five days after completion of NP dosing in press mesocosms (day 30 of experiment), aqueous concentrations of Ce had declined to an average of 0.46 mg/L, which was still higher than any Ce concentration measured in the pulse-dosed stream. Consequently, the concentration of Ce in periphyton was lower in the press-dosed stream on day 30 (average of 9.08 µg/g of dry sample) than in the pulse-dosed stream (average of 13.11 µg/g). The press dose resulted in longer-range transport of NPs, such that periphyton concentrations of Ce in the lower reaches of the press-dosed stream were nearly double those observed for the pulse-dosed stream (6.4 µg/g vs. 3.3 µg/g, respectively), likely because of a reduced particle-particle interaction and subsequent aggregation relative to the pulse addition. These results suggest that exposure scenarios may play a significant role in determining the environmental fate, transport, and bioavailability of stable metal oxide nanoparticles.

Development of fertile magma at El Teniente, Chile: Implications for porphyry-style mineralisation

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El Teniente porphyry Cu-Mo deposit is located in the Andean Cordillera in the central Chilean porphyry belt, which is host to a number of world-class late Miocene-Pliocene porphyry copper deposits. El Teniente is considered one of the world’s largest copper deposit in terms of contained metal, with a total identified resource of over 16 billion metric tonnes (Gt) at 0.554 % Cu [1] and 7.8 Gt at 0.018 % Mo [2].

A series of calc-alkaline intermediate to felsic porphyritic sills and dikes, collectively termed the Teniente Plutonic Complex, are spatially associated with magmatic-hydrothermal breccias and veins that host mineralization at El Teniente. They were emplaced between 7.1-4.9 Ma, although previous work has suggested a 7.10 ± 0.41 Ma age for a sample of the porphyry may be inherited [3,4].

Samples from the Teniente Plutonic Complex have been analysed for Rb/Sr and Sm/Nd isotopic compositions. εNd values are consistently positive, ranging from 2.4 to 3.2, whereas ⁸⁷Sr/⁸⁶Sr values are between 0.70388 and 0.70421. When compared to other intrusive rocks from Central Chile [5], El Teniente rocks display broadly similar trends, implying that a geologic event led to an abrupt decrease in εNd values ca. 5 Ma. The isotopic data reflect localized assimilation of crustal material into the mantle wedge as a result of subduction erosion adjacent to a zone of ridge subduction [5], rather than intra-crustal contamination, consistent with a subduction-erosion model [6]. The data suggest the Teniente Dacite Porphyry and associated mineralization was emplaced as several discrete intrusions over a ca. 1 million year period. This process has implications for the relationships between porphyry emplacement and Cu-Mo mineralization in central Chile.

Volatiles are responsible of magma ascent from reservoir to surface. For differentiated melt, H$_2$O is the main volatile species, the behavior of which control the eruptive style. But H$_2$O is generally difficult to measure precisely that limits the dataset available. Halogens are interesting to study and particularly Cl that is easier to analyse in volcanic glass (residual glass and melt inclusions) by electronic microprobe at the concentrations that occurred in natural samples.

Cl is generally controlled by its partitioning into the H$_2$O phase that explains a wide range of behavior. Here we present different results on Cl behavior in magmas, from basic to acid composition, in order to highlight how Cl may be a useful parameter for degassing processes. In rhyolitic melt, Cl follows H$_2$O behaviour and provides the same information of closed- vs. open-system degassing. In alkali magmas such as phonolitic or trachytic magmas, Cl content in magmatic melt may be buffered in precisely (P, T, composition) domain corresponding to magma storage at depth in equilibrium with a volatile element and images a stratified reservoir. Whatever the composition, effective Cl degassing potentially affecting the environment.

We illustrate these different behaviors with data on glass (melt inclusions and residual glass) from different eruptions (Vesuvius, Etna, Azores, Lesser Antilles and Vanuatu arc).

Cyclic dolomitization of limestone at Oker (Germany)

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Magnesium and sulfur are one of the major elements that control dolomitization in marine, low-temperature environments. However, conditions and reaction mechanisms, which are related to dolomitization are poorly understood.

We investigated partly dolomitized limestone (Oker, Langenberg, Germany) of Upper Jurassic age (~153 Ma) that was deposited in a shallow marine, sabkha environment. X-ray diffraction (XRD), $\delta^{18}$O and $\delta^{13}$C isotope measurements, and electron microprobe (EMP) analyses were completed on porous dolomite, sandwiched by layers of limestone.

The lower limestone layer consists of micritic calcite (-1.7 to -2.9‰ of $\delta^{18}$O and 1.3 to -0.7‰ of $\delta^{13}$C, VPDB), which formed under marine conditions. EMP analyses revealed low-Mg calcite (LMC) of (Ca$_{0.96-0.99}$Mg$_{0.004-0.03}$Sr$_{0-0.01}$Na$_{0-0.01}$Fe$_{0-0.02}$/0.90-1.0CO$_3$). Samples from the contacts between dolomite and limestone layers contain LMC, high-Mg calcite (HMC), and dolomite, which are associated in single grains. The dolomite core, (Ca$_{0.97-1.14}$Na$_{0.01}$/0.97-1.0CO$_3$, Mn$_{0.002}$/0.01), is ~10 μm in diameter, and is surrounded by LMC, (Ca$_{0.95}$/0.01Na$_{0-0.01}$/0.99CO$_3$), and subsequently deposited HMC, (Ca$_{0.94-0.97}$Mg$_{0.04}$/0.93Fe$_{0.04}$/0.99Na$_{0-0.01}$/0.98-1.0CO$_3$), and shows alternate growth zones of S and Fe.

XRD data confirm non-stoichiometric dolomite with 1-54 mol% of CaCO$_3$. The degree of order in dolomite, in respect to dolomite super structure, decreases from 83% to 42% with increasing S contents from 0.02 to 0.06 S [a.p.f.u.], respectively. The upper limestone layer contains no dolomite or HMC, and displays marine conditions; i.e., micritic LMC (-1.8 to -4.0‰ of $\delta^{18}$O and 1.3 to -0.7‰ of $\delta^{18}$C, VPDB).

The euhedral shape and the (Fe, S)-growth zoning of the dolomite crystals, and the alternate zones of dolomite, LMC, and HMC suggest dolomitization via dissolution of primary carbonates and subsequent cyclic and abrupt changes in the chemical (Mg, Fe, and S), and isotopic composition of the interstitial solutions.
A distinct tectono-metamorphic evolution at the southern edge of Tisia Mega-Unit revealed by monazite and xenotime age dating

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The Slavonian Mountains (Pannonian Basin, Croatia) are the area of particular significance within Tisia Mega-Unit. This large unit, with complex internal structure, encompasses three huge southward dipping Alpine nappe systems that expose characteristic lithologies of south-eastern part of Pannonian Basin basement. Complexes of the central nappe system (i.e. Bihor) outcrop along the 5.5 km long, NNW–SSE trending Kutjevačka Rijeka transect. This transect is one of the most prominent geological cross-sections that reflects a complex history of the metamorphic and igneous evolution, giving insight into crustal evolutionary processes and their relationship to deformation and metamorphism.

Our previous age dating of monazite from the representative rock complexes along Kutjevačka Rijeka transect, combined with geothermobarometric data, revealed complex structure and metamorphic history that includes a pre-Variscan (Ordovician to Silurian: 44±19 and 428±25 Ma) and a Variscan (356±23 Ma) medium-grade metamorphism [1, 2]. The primary focus of this study is on surprisingly large extent of very low- to low-grade Alpine metamorphism recorded in the parametamorphic rocks (chloritoid and chlorite schists) along the transect. The Th–U–Pb age dating on xenotime grains within the chloritoid and chlorite schists along the transect. The Th–U–Pb age dating on xenotime grains within the chloritoid and chlorite schists revealed two peaks at 113±20 and 82±23 Ma. Those ages argue against "stratigraphic doubts" that contradict obtained ages shows two peaks at 120 and 80 Ma while age of 120±36 Ma, peak metamorphic conditions reaching 3.5–4 kbar and 340–380 °C. The age of 219±81 Ma obtained age of 219±81 Ma obtained on Yb-rich xenotime (inherited?) core domain(s), implies a possible existence of older low-grade metamorphic phase(s) [3]. Two distinct penetrative low-grade metamorphic foliations recorded in the chlorite schists are accompanied by existence of two populations of small (~3.5 µm) low-Th monazites, giving an average age 99±15 Ma. Histogram of obtained ages shows two peaks at 120 and 80 Ma while age modelling recognized two peaks at 113±20 and 82±23 Ma. Those ages argue against "stratigraphic doubts" that contradict Alpine metamorphism in the area.


Contribution of fungi and bacteria to the Mg biogeochemical cycle in podzolic soils

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Silicate mineral weathering is a key process in soil formation through leaching of essential elements (Mg, Fe, Al), which sustain plant growth and determine the chemistry of soil solutions and exchange complex. Biological role on silicate mineral weathering remain to date a scientific challenge due to the strong relation between plant growth, silicate mineral weathering and CO₂ cycle. However, some constrains, such as microflora associated to plants, are unresolved allowing to quantify biological impact on silicate mineral alteration in the soil and on major cation biogeochemical cycle. Soil microorganisms (fungi and bacteria) play a major role in the availability of nutrients in soils. They participate in weathering of primary materials through the production of low-molecular masses organic acids (LMMOAs). The objective of this study is to quantify the impact of microorganisms (bacteria and fungi) during granite bioweathering and to better understand and quantify the contribution of microflora to Mg biogeochemical cycle.

For this, we lead several experiments of geological material (granite) bioweathering to investigate the impact of fungi and bacteria on the release of Mg from granite during 42 days. The microbial communities were directly isolated in November 2011 from different horizon (O, E, B) of a podzolic soil under 3 different tree species (Scots Pines, Spruce, Birch) in Norunda (Sweden). To characterize mechanisms of dissolution, we monitored low-molecular organic molecules produced by microorganisms, microbial biomass, pH, Mg released and Mg isotope ratio variations.

Result indicates that pH decreases significantly from 6.5 to 4.5 during the first week of the experiments and then roughly stabilizes over time. In contrast, in all experiments, the fraction of released Mg is strong until 30 % at the end of the experiments. There is a positive correlation between the Mg leached from phlogopite and the carbon produced from the upper part of the organic horizons of the soil are less efficient to weather the granite and don’t produce great quantities of LMMOAs. Preliminary isotope analyses indicate that δ²⁶Mg in the leaching solutions collected at the end of the experiments are close to the initial value of the granite. Only leaching experiments performed with microbial communities isolated from the upper part of the organic horizons induce a high enrichment in the light isotope (~ -1.0‰) in the solution, suggesting a biotic effect that will be investigated.

DOI:10.1180/minmag.2013.077.5.2
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Combined Halogen (Cl, Br, I) and noble gas mantle geochemistry

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Not yet two decades ago the community view of the mantle structure had converged on a mantle geochemically layered at 670km depth. This model has passed on, is no more, ceased to be, expired and is now history. Killed, by geophysical observation. Although the layered mantle is now an ex-model the geochemical observations used to support it remain; the formation, location and evolution of a volatile rich mantle reservoir capable of fluxing the mantle beneath mid ocean ridges with accretionary volatiles, such as 3He, still attracts significant attention.

High precision multi-collector noble gas mass spectrometry is providing us with new detail of the mantle system. MORB basalts and mantle-derived CO2 natural gas fields show a MORB-source mantle with light and heavy noble gases, and therefore associated volatiles, that originate as a trapped component in accreting meteorites [1]. New data from Iceland nevertheless, shows that the Iceland OIB source region is incompatible with this source simply providing the noble gases now in the upper mantle [2]. An additional volatile input into the mantle is today through recycling noble gases with a seawater signature [3], while dry subduction may have operated on the Early Earth to introduce accretionary volatiles into the mantle [4].

Heavy halogens (Cl, Br, I), in combination with noble gases, are a powerful tool to understand the subduction of volatiles and highly incompatible elements in detail [5]. Due to low Br and I concentrations, new techniques only now allow us to determine: accretionary material characteristics; partitioning data; and investigate the different terrestrial reservoir halogen mass balance. We present an overview of progress in this new field and discuss how the combined halogen/noble gas data might be used to reconcile the apparent need for a volatile-rich reservoir that fluxes the shallow mantle with the new Icelandic data [2].


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org

Reconstructing the Rheic: Geochemical analysis of ocean lithosphere from the Variscides

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Although the Rheic Ocean dominates palaeo-geographic reconstructions of central Europe during the Palaeozoic, many factors regarding its general evolution & internal tectonic configuration are inadequately constrained [1]. A major component in aiding a better understanding of these factors is the accurate assessment of suture zones & associated metabasite suites within the internal Variscides. As such this study focuses on the geochemistry of the Lizard- Cornwall, Sudetes-Poland, Acatlan-Mexico & Ossa-Morena, Careon, Morais-Iberian ophiolite complexes. Sampling within these complexes focused on the least deformed mafic members in order to fully assess the geo-tectonic setting of basalt genesis. Major, trace and rare earth element data (XRF & ICP-MS) has been examined and shows general LREE depletion & a lack of significant Ta, Nb or crustal derived element anomalies for all complexes. The new geochemical data enables an accurate discrimination of the geo-tectonic setting for each complex and aids in constraining future palaeo-geographic reconstructions of the enigmatic Rheic basin. The lack of crustal contamination & origins within the upper mantle, facilitates use of some samples for a future Hf-Nd isotope study aimed at fingerprinting the Devonian upper mantle and furthering our understanding of the origin & evolution of the Dupal anomaly [2]. Additionally, we will use the isotope data to investigate models to explain the apparent depleted nature of the source of Rheic Ocean basalts [3].


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Clumped isotope thermometry in Belemnite shells from the Early Cretaceous Karai Shale Formation, Trichinopoly, India

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Well-preserved Belemnites fossils are hosted in the upper Albian Karai Shale Formation, India, which represents an offshore high stand depositional environment (1,2). It has been argued that δ18O variability in these Belemnites – growth bands reflect seasonal –paleo-temperature changes in the sea water (2). We investigate paleo-seawater temperatures by analyzing clumped isotopes (Δ47) in 15 petrographically and chemically well-characterized unaltered samples of Belemnite guard shells. Sample powders were drilled from the exterior growth bands, avoiding the outermost portion. δ18O and δ13C were also determined. Our Δ47 measurements yield a temperature range of 20°C (Δ47 = 0.667±0.005) to 42°C (Δ47 = 0.624±0.005) using the Ghosh et al., (2006) thermometry equation. The spread in Δ47 values together with δ13C and δ18O and inferred salinity values allowed characterization of the 15 samples into three suites with distinct temperature and salinity ranges. Considering the nektonic behaviour of Belemnites (3), we propose an alternative mechanism to explain the spread in our paleo-temperature data by invoking the role of thermohaline circulation during Early Cretaceous, similar to modern mid-latitude modern oceanic conditions.


Major and trace element geochemistry in groundwater of Patancheru Industrial Area, Andhra Pradesh, India

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Patancheru Industrial Development Area is located about 40 km from Hyderabad City, A.P. This is one of the contaminated areas identified by the Central Pollution Control Board (CPCB) New Delhi. More than 200 small and large-scale industries manufacture pharmaceuticals, paints, pesticides and chemicals and metallic products in this region. All effluents drain through the area to join the main Nakkavagu stream, which merges into Manjira River, and is one of the major drinking water sources to some parts of Hyderabad and adjoining areas.

During pre- and post-monsoon seasons the ground water samples were collected from open and bore wells. The samples were analysed for major, minor and trace constituents. Several heavy and toxic trace elements were estimated by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The geochemical data obtained was utilized to assess the extent of pollution and its impact on human health. Some of the toxic and trace elements (As, Se, Pb, Cr, Cu and Mn) were found to be more than the desirable levels in drinking water (WHO guidelines). The Contour maps for these trace elements were prepared to know their spatial and temporal distribution and to identify the point source and transport of the contaminant. These studies would emphasis the need to adopt some remedial measures and combat pollution.
Geochemical characteristics and correlation of oil-source in Minfeng area for Dongying depression, Bohai Bay Basin, Eastern China

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The Minfeng area is located in the northeast of Dongying Depression. The characteristics of the gas chromatography of saturated hydrocarbons and the steroid terpane biomarkers show that there are three sets of source rocks with obvious differences including the upper part of the fourth member of the Shahejie Formation (simplified as Es4s), the middle part of the third member of the Shahejie Formation (simplified as Es3x), and the lower part of the third member of the Shahejie Formation (simplified as Es3x). There are four types of oil.

Further studies focus on oil-source correlation. Based on the techniques of fingerprint indetification, scatter diagram analysis and mathematical statistics, the results indicate that oils in reservoirs of the second member of the Shahejie Formation (simplified as Es2) from 7 to 10 sand units of Yong3 fault-block, Es2 (No.4 sand unit) of Yong5 fault-block and Yanjia area came from Es4s source rock. Oils in reservoirs of Minfeng sag came from Es3x and Es3z source rocks. Oils in reservoirs of Es2 (No.3 and No.5 sand units) of Yong3 fault-block, Yong66 fault-block, Yong12 fault-block, Yong51 fault-block are mixed by oils coming from Es4s and Es3x. Oils in reservoirs of Es2 (No.3 and No.5 sand units) of Yong2 fault-block, Yong63 fault-block came from Es3x source rock.

It is possible to infer that oils from Es4s source rock, which were main along the favorable sandbodies and unconformity, migrated laterally from sag and Yanjia area and eventually filled in the sandy conglomerate bodies of Es3 and Es4 because of lack of oil-source faults. Oils are diverse types because of many oil-source faults in Yong Anzhen area. It implies that traps in Yonganzhen area formed in the same period according to the distribution of the types of oils on the plane. Early generated oil accumulated in the reservoir which was near to the source rocks. With the further burial depth of the source rocks, overlying source rocks gradually entered the hydrocarbon generation period, the oil began to accumulate in traps which were further distance from the source rocks.

Direct atmospheric $\text{O}_3$ and $\text{O}_2$ signatures from the deep past and their first-order pattern

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The isotope compositions of atmospheric $\text{O}_3$ and $\text{O}_2$, two of the most important molecules in the atmosphere, offer us windows to the deep history and evolution of the Earth. Sulfate is an oxygenion capable of recording direct $\text{O}_3$ and/or $\text{O}_2$ signatures from the distant past. Recently, an improved understanding of the triple oxygen isotope systematics of various sulfur oxidation processes has demonstrated that secondary atmospheric sulfate bears $\text{O}_3$ signature ($\Delta^{17}\text{O}$ positive), while sulfate of oxidative weathering origin bears $\text{O}_2$ signature ($\Delta^{17}\text{O}$ negative). The ultimate source of the $\Delta^{17}\text{O}$ anomalies in $\text{O}_3$ and $\text{O}_2$ is the Chapman reaction in the stratosphere, which via stratosphere-troposphere exchange links the concentrations and triple oxygen isotope compositions of atmospheric $\text{O}_3$, $\text{CO}_2$, and $\text{O}_2$ to the rates of bioproductivity, weathering, and organic burial on the Earth surface.

Despite many unfilled gaps in its record, I propose here that, from existing data, a first-order temporal pattern for sulfate $\Delta^{17}\text{O}$ for the last 3.5 billion years has emerged. There are three outstanding features. (1) The Marinoan O-17 Depletion (MOSD) event at 635 Ma is a clear anomaly in which the $\Delta^{17}\text{O}$ of sulfate reached as negative as $-1.64\%$. The most viable explanation for this event is a post-glacial, ultra-high pCO2 world, which is consistent with the “snowball” Earth hypothesis. Data for other alleged “snowball” Earth periods are lacking at this time, and other secondary “depletion” events are predicted. (2) The Archean sulfate has an average $\Delta^{17}\text{O}$ value of $-0.05 \pm 0.05\%$, while the post-Archean sulfate has an average $\Delta^{17}\text{O}$ at $-0.12 \pm 0.05\%$ (MOSD data excluded), a pattern that is consistent with the loss of $\text{O}_2$ shield, i.e. the absence of Chapman reaction, in the Archean. However, the role of thermal alteration has yet to be examined. (3) The oldest sulfate with distinct positive $\Delta^{17}\text{O}$ values has been traced back to the Eocene (~35 Ma). However, if $\text{O}_2$ became essential in atmospheric oxidation of SO2 as soon as the $\Delta^{17}\text{S}$ anomaly ceased to exist in rock records, $\Delta^{17}\text{O}$-positive sulfate should have been produced since the Early Proterozoic Era. Bear in mind that any geological record is the net result of production and destruction. By understanding the geologic context of sulfate records, and by exploring diverse and continental deposits in particular, we shall piece together a first-order, direct geological record of atmospheric $\text{O}_3$, $\text{O}_2$, and $\text{CO}_2$ for the last 3.8 billion years.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
U-Pb dating of hydrothermal zircon and its implications for the metallogeny of the Dongping gold deposit in North China

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The large Dongping gold deposit is located in the northern margin of the North China Craton, northwestern Hebei province, China. The ores are hosted by the Shuiquangou syenite complex and consist mainly of auriferous quartz veins and K-feldspar altered and silicified disseminated ores, both of which are characterized by low sulfide volumes, Te-rich and As-poor. U-Pb dating of zircons from the hornblende syenite on the western margin of the complex yields an age of crystallization of 400±3.5Ma. The close spatial relation of the gold mineralization with the syenite complex, and S, Si, and Pb isotope compositions of the ore-related minerals, suggest that the ore deposit might be genetically related to the syenite complex. However, almost all of the published age of ore-formation vary in range of 157~177 Ma (⁴⁰Ar-³⁹Ar ages of hornblende). The hydrothermal zircons from the first stage disseminated ore and grey auriferous quartz vein are dated at 389±1.0Ma and 385±5.7Ma, respectively, which are close to the crystallization age of the syenite complex and might have been formed during post-magmatic hydrothermal processes. Considering the two type of ores are dominant parts of the ore deposit, we argue that the pervasive post-magmatic hydrothermal alteration is the main ore forming stage. U-Pb dating of the hydrothermal zircon from the low grade auriferous quartz vein yields an age of ~140Ma, which represents Yanshannian hydrothermal superimposition. Thus, the Dongping gold mine is a post-magmatic hydrothermal ore deposit with later stage hydrothermal overprint.


Distribution of rare earth elements in marine Co-rich ferromanganese crusts of the South Atlantic

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Rare earth elements (REE) are of great geological, technological, economic and strategic interest. The increasing use of REE in high-tech products and the restrictive politics of some countries for commercialization of some REE raw products resulted in search for new deposits of these elements as well as the feasibility of unexplored reserves. One of the possible sources of REE are cobalt-rich seamount ferromanganese crusts. These are unconventional ores abundant in the deep ocean. Co-rich crusts are enriched in metals such as Co, Pt, REE, Ti, Ni, Tl, Te, Zr, W, Mo and Bi. The chemical and mineralogical characterization of Co-rich crusts occurrences has been carried out in several oceans [1,2]. In the South Atlantic, they are well known in the Rio Grande Seamount [3]. Ferruginous vermicid is a common phase in Co-rich crusts and moderate amounts of carbonate-fluorapatite (CFA) are found in thick crusts, as well as low amounts of quartz and feldspar[4].

In this work, samples of cobalt-rich crusts from the Rio Grande Seamount, South Atlantic were chemically characterized. Trueness of analytical data was checked by analysis Co-rich seamount crust reference materials GSMC-1 and GSMC-3 [5]. The content of REE in the analysed samples is variable (ΣREE 320-3,100 mg/kg) and only 5-10% of these totals it is of heavy REE. Almost all samples show strong enrichment in Ce, as evidenced by PAAS normalized REE patterns. Such type of finding was previously interpreted as related to hydrogenetic Fe–Mn crusts [6]. Their formation is ascribed to the oxidative scavenging of Ce and its preferential removal from seawater by hydrous Fe–Mn oxides.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
On regularities in accumulation and distribution of elements in living matter of natural and technogenic ecosystems

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The task of gaining information on element composition of living matter was set by V.I. Vernadskiy at the beginning of the last century. In spite of the long history of study in this problem, there is still a number of questions to be answered.

For this purpose we have revealed the regularities in accumulation and distribution of elements in living matter on the sites with various rates of natural-technogenic ecosystem transformations. The research is based on the results of up-to-date high-sensitivity analytical methods – instrumental neutron activation and inductively coupled mass-spectrometric plasma (ICP-MS).

Living matter is not homogeneous in its composition. The analysis of materials obtained by us attests the fact that in regularities of element mean content distribution in living matter the conformities of their accumulation are observed that correspond to general distribution laws for material objects: that of Mendeleyev-Clark on element distribution in different masses and Oddo-Harkins rule on element interchange with even and uneven numbers. It was revealed that in the zones of geochemical abnormalities conditioned by geologic and metallogenetic features there is an increase in concentration of specific elements in composition of living organisms against the background of observing geochemical regularities. Element composition of living matter is subjected to significant transformation in the zones of technogenesis. In such zones the disruption in basic element accumulation regularities is observed. As a result it was stated that technogenic factor has an effect on organism of modern urban residents in the form of intensive accumulation of such elements as lead, gold and cadmium.

The results of research in living matter from different sites shows that the indicators of its internal changes under the influence of the environment are mostly the element relationships. The most informative is Tb/U, as well as the relationship of rare-earth elements and some others.

Geochemistry of mineral springs ecosystems of Baikal region

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The Baikal rift area is characterized by a rich variety of mineral springs. The research of microbial communities has been started quite recently, but there is a lot of information showing the important role of microbial communities of hot springs in the evolution of life in the Precambrian [1].

The complex studies in thermal springs have shown that severe environmental conditions (high temperature, alkaline pH and high sulfide content) contribute to the development of specific microbial communities, having significant biodiversity and high intensity of biogeochemical processes, comparable to the microbial communities of neutral thermal spring. The main feature of these communities is the formation of microbial mats, often in collaboration with travertines [1].

The objective of our study is to identify geochemical features of different springs in the Baikal rift area. Thus, the mat samples were taken in several springs of the Baikal region in the summer of 2012. The chemical composition was determined by multi-element neutron activation analysis (Department of Geoecology and Geochemistry of Tomsk Polytechnic University, Russia).

The data shows that the mats of different mineral springs are characterized by absolutely different content of elements. Thus, mats of the tonic spring are characterized by the largest content of Na, the mats of methane spring – that of Ca. The mats of some springs are characterized by higher content of some elements. For instance, the mats of cold Arangatuy stream have higher content of Ba, Ce, Nd, Th, Tb, Yb, Ta, Sm. We should bear in mind the higher accumulation of the mats in the stream of U (177 mg/kg).

All this suggests that the mats help to assess biogeochemical role of microorganisms in ecosystems, shows an important role of microbial communities in hot springs in the evolution of life on the Earth, as well as taking an active part in the formation of travertine [1].

Petrological constraints on formation of the martian crust

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The 4 Ga-record of Martian volcanic activity has been characterized over the last decade by various remote sensing instruments, including gamma ray spectroscopy and visible/near-infrared spectroscopy. Based on these data, the narian crust is viewed as a basalt-dominated world with limited crustal differentiation. This relatively simple situation (when compared to the Earth) may be responsible for observed trends in surface chemistry and mineralogy with age, such as an increase with time of the abundance of high-calcium pyroxene relative to that of low-calcium pyroxene. Indeed, petrological modeling suggests that these trends can be explained in terms of variable degrees of partial melting of a mantle of constant composition [3,4], providing a quantitative estimate of the average cooling rate of the martian interior. On the other hand, further work is needed to reconcile this model with the existence of distinct geochemical mantle reservoirs inferred from the analysis of the SNC meteorites. The idea that the martian mantle has been cooling for at least the last 4 Ga, as constrained from data spanning the entire Noachian-Hesperian-Amazonian periods, has several petrological, geochemical and geophysical implications. For example, mineralogical transitions observed around 3.7 Ga (when compared to the Earth) may be responsible for observed trends in surface chemistry and mineralogy with age, such as an increase with time of the abundance of high-calcium pyroxene relative to that of low-calcium pyroxene. Indeed, petrological modeling suggests that these trends can be explained in terms of variable degrees of partial melting of a mantle of constant composition [3,4], providing a quantitative estimate of the average cooling rate of the martian interior. On the other hand, further work is needed to reconcile this model with the existence of distinct geochemical mantle reservoirs inferred from the analysis of the SNC meteorites.

Hydrogeochemical and isotopic characterization of the Saturnia thermal aquifer

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The thermal area of Saturnia was discovered and visited for several centuries before the Roman Empire and is still one of the most visited thermal springs in the world. It is located in central Tuscany between the Monte Amiata and the Tuscan volcanic area to the south. Herein, we study the thermal aquifer by chemical and isotopic analyses.

At first time, chemical-physical analyses have been used to a preliminary choose between all the sampled waters. Later, some elements and compounds (Na, Ca, Mg, K, Cl, SO42-, NO3-, total alkalinity, Li, Sr, B, F, SiO2, CO2, Sb, As, Se, Fe, Mn, Hg e Pb) have been analyzed ad used to classified the previously chosen samples. In particular, Lithium (according to [1]), Boron and Strotium shows that the main important host of the studied thermal water is the calcareous geological formation of "Calcare Caverno"; high values of Selenium, according to [2, 3], also shows the influence of volcanic fluids in the thermal anomalies of the Saturnia thermal area.

Finally, some isotopes have been analyzed (2H; 3H, 3He,3He, 14C, 18O, 86Sr, 87Sr) to obtain others important information. The isotopes in the water molecule show that the recharge area of the thermal aquifer is located some km towards north regarding to the Saturnia spring, and his residence time is greater than 30 years. The 87Sr/86Sr ratio, measured in the Saturnia thermal water, allowed distinguish the aquifer (according to [4]) from the other host of the near thermal aquifer of Mt. Amiata, sampled in Bagl Pi Filippo. The isolation from the surface infiltration during the underground flow of the thermal water of Saturnia has been checked by the values of δ18O. And by the analysis of 3He/4He, sampled in a larger area, the influences of the mantle in the Saturnia thermal area has been excluded, in according to [5].

Probing the interactions between iron oxides and sediment organic matter using X-ray absorption spectroscopy

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Sediments and sedimentary rocks make up the largest sink for organic carbon on the planet while approximately 20% of the organic carbon found within marine sediments is bound to reducible iron oxide species [1]. Here we use Scanning Transmission X-ray Microscopy (STXM) as well as X-ray Absorption Near Edge Spectroscopy (XANES) in order to probe the local environment of iron oxide-bound organic matter within a variety of marine surface sediments and water column suspended particles. STXM data was collected on beamline 10ID-1 (SM) at the Canadian Light Source, where we analyzed regions with iron co-localized organic carbon, and then obtained spatially relevant NEXAFS images and spectra for these regions at both the carbon K-edge and iron L2,3-edge. From these we are able to determine the speciation of both carbon and iron with a spatial resolution of 40 nm. We see important contributions from aromatic and carboxyl functionalities independent of the presence of iron but see an increase in the relative proportion of aliphatic functionalities in the presence of iron-organic mineral phases.

XANES spectra at the iron K-edge were collected at beamline X26a at the Brookhaven National Synchrotron Light Source and were used to probe the effect bound organic matter has on the X-ray absorption spectra of iron. A shift towards lower energies was seen at the iron edge for synthetic iron oxides precipitated in the presence of organic matter, demonstrating that we can distinguish between iron oxide-bound organic matter and pure iron oxide minerals. XANES spectra were also collected on a variety of surface sediment samples; using linear combination fitting and well-defined end-members, we were able to determine the proportion of sediment iron which is bound to organic matter based on the effect of organic matter on the synthetic iron co-precipitates.


The role of iron in the diagenesis of organic carbon and nitrogen in sediments: A long-term incubation experiment

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The burial and preservation of organic matter (OM) in marine sediments is tightly coupled to the diagenetic cycles of iron and manganese. These strong iron-OC complexes, formed within the oxic layer of the sediment, are transferred to the deeper anoxic sediment layers through sedimentation, physical reworking and bioturbation; and are metastable over geological timescales [1]. Using a long-term (400-day) incubation, we examined the effect of iron on the early diagenetic transformations of OM in marine sediments. The fate of fresh, algal-derived DOM was monitored by tracking its stable carbon isotopic signature (δ13C). We demonstrate the incorporation of the 13C-depleted tracer into the sediment through sorption (adsorption and co-precipitation with iron oxides). In the presence of iron oxides, we observed increased transfer of the dissolved algal material to the solid phase, revealing the role of iron in shuttling OM from sediment porewaters to sediment particles. Furthermore, we show that the presence of iron has a differential effect on OC and organic nitrogen (ON), with preferential preservation of OC and accelerated degradation of ON in the presence of reactive iron oxide surfaces. Hence, we propose that redox-sensitive metals may play a crucial role in regulating the global redox balance through increased carbon preservation as well as controlling the concentration of reactive nitrogen species in the open ocean.

U behaviour under acid mine drainage conditions: Preliminary results from an experimental approach in Río Tinto area (Spain)

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Preliminary results show that dissolved U and Th concentrations in water samples collected from Río Tinto area is 2-3 orders of magnitude higher than that in the environmental base-levels in undisturbed areas with 234U/238U activity ratios (UAR) much higher than 1, thus indicating a strong disequilibria. Taking into account that under low pH conditions, congruent dissolution rates are high, this disequilibrium is surprising. Different waste pile rocks that include bedrock Fe oxihydroxides, gossans and country rocks have been used for conducting a set of leaching experiments. Results indicate that: 1) Distilled water leaching, although creating an acidic media very rapidly, do not generate leachates with UAR higher than 1.8 in most cases UAR being close to unity; 2) Leaching with different mixtures of acetic acid and ammonium oxalate lead to very high UAR ratios in leachates from Fe-bearing ochre bedrock sediments; 3) Sulphuric acid leaching experiments also generate leachates with high UAR ratios in Fe-rich materials, this not being dependent on acid concentration; and 4) Sulphuric acid leaching after annealing of Fe-oxihydroxides at 800°C during several hours results in leachates with UAR close to unity. All these results indicate that not only the leachant but also the extent (?) of radiation damage in Fe-oxihydroxides play an important role in the origin of U isotope disequilibrium under acidic conditions.

Melting of an hybryd source below the Danakil Region

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The Danakil region is a modern example of rifting located atop a mantle plume. Along the rift system, a large number of shield volcanoes erupted large volumes of tholeiitic magmas with a wide compositional range, generally enriched in incompatible and trace elements, reflecting the source heterogeneity and the variability of melting processes that contributed to their generation. The Danakil lavas represent the combined product of continental rifting and ascending mantle plume processes.

Major and trace elements were analyzed in modern lavas sampled from the Erta Ale Chain and the Asal region and compared to literature data. Although highly enriched in trace elements, our lavas are significantly different when compared to the Oligocene main lava suites generated in the earliest stages of mantle plume activity. Based on La/Sm, Rb/Sr and Zr/Nb ratios and REE abundances they are intermediate between the high-Ti primitive lavas and the low-Ti tholeiitic basalts erupted 30 Ma ago due to the arrival of the plume-head. Trace elements abundances and geochemical modelling indicate that our lavas derive from a “hybrid” source characterized by a great complexity, possibly a metasomatized sublithospheric-mantle component that includes hydrous phases and melting at depths lower than those that generated the Oligocene lavas.

The wide compositional range of the Afar lavas suggests that those modern lavas erupted along the rift are not simply the product of melting of a deep mantle plume but derive from a composite source resulting from the interaction between the plume tail and the surrounding sublithospheric mantle previously metasomatized by the plume activity. As a consequence, this very complex and heterogeneous source undergoes extremely variable melting processes as testified by the characteristic chemistry of each volcanic complex.

Further geochemical and isotopic investigations will help to better constrain the signature and contribution of each of the reservoirs and to what extent the mantle is metasomatized by hydrous phases below the Afar region.
Geochemical analysis of the pigments and affinity of the Jurassic calcareous algae Solenopora jurassica

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The enigmatic fossil calcareous algae Solenopora jurassica is known for its distinctive pink and white banding. Though widely accepted as an algae, there has been some debate over its taxonomic affinity, as well as the derivation of its visible banding pattern which though to be seasonal. Despite these hypotheses little geochemical work has been carried out to test them. This study represents the first in-depth geochemical analysis of this fossil in order to study its affinity and the possible seasonal origin of its banding pattern. Seasonal growth is shown by differences in calcite density, and increased Mg/Ca molar ratios and chlorine levels indicate higher temperatures during the time that white bands were deposited when compared to the pink bands. Pyrolysis gas chromatography mass spectrometry and infrared spectroscopy show the presence of tetramethyl pyrrole and carboxylic acid groups, indicative of the red algal pigment phycocyanin. This supports the identification of S. jurassica as an algae, given that the pigment is only known to occur in cyanobacteria and algae. There is no evidence that the fossil is bacterial and no other taxonomically indicative biomarkers were identified.

Serpentinites as catalysts for vapor conversion of methane in the Earth crust

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Serpentinites of the oceanic lithosphere are an active source of reduced gases, such as H₂, CH₄, as well as an abiogenic source of complex hydrocarbons. Appearance of H₂ is related to the serpentinization of ultrabasic rocks of the oceanic floor. However, production of H₂ in the CH₄ and H₂O-bearing fluids is possible according to the catalytic reaction known as «vapor conversion of methane», since serpentinite composition and structure can serve as close analogy of the artificial catalysts. We performed an experimental study of the reaction of the methane conversion by vapor using massive lizardite-antigorite serpentinite, which in addition to serpentinite contains chromite, magnetite and few chlorite. The sample has not crushed to the fraction 0.5-0.7 mm before experiment. The volume ratio H₂O/CH₄ in the reaction zone was 8-10/1, filtration rate through the rock 1 cm-s, while the time of the contact of the vapor-methane mixture with serpentinite was 1.5-2 s. During interaction with the vapor-methane mixture, serpentinite was partially dehydrated with presumable formation of olivine and silica-rich aqueous solution. Chromatography shows that the conversion of CH₄ to H₂ increases with temperature and reaches 14 % at 825°C. The conversion of CH₄ to CO and CO₂ at 825°C is 3 % for both components. Along with H₂, CO and CO₂ the reaction products include ethanol and methanol, which do not form on standard catalysts. The present experimental results support the conclusion on the high catalytic effectiveness of serpentinite: at short time of contacts of the vapor-methane flux with this rock resulted in relatively high degree of conversion. Experiments inspire testing of the catalytic properties of other crustal rocks.
Spatially resolved fully simultaneous determination of large numbers of isotope concentrations and isotope ratios by LA-MH-ICP-MS

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Laser Ablation-ICP-MS has developed into a powerful tool for the determination of elements, element ratios and isotope ratios in solid samples. The analysis of more and more elements with high spatial resolution and from ever smaller sample sizes is a challenge for this technology.

The development of a fully simultaneous ICP-MS brings several advantages for resolving this challenge: ‘all’ elements and isotopes can be determined in the same analytical run without sacrificing analysis time for any isotope. The simultaneous measurement also allows elimination of correlated noise, like flicker noise from the plasma or noise generated by the ablation process itself.

Figure 1: Mattauch-Herzog MS with Solid State Detector.

A double focussing sector field mass spectrometer in Mattauch-Herzog (MH) geometry (Figure 1) was combined with a 4800-channel, large CMOS based semiconductor direct ion detector, placed in the focal plane of the magnet. Each of the channels operates fully simultaneously, using two different amplifications, covering the mass range from ~5 to 240 amu.

The use of this new technology with laser ablation, for simultaneous chemical imaging of large numbers of isotopes, and analytical results for relevant samples, will be presented, with special emphasis on the expected advantages of the fully simultaneous detection.

Microstructures and compositions of melt inclusions from Jubrique (S Spain): Implications for anatexis

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Melt inclusions (MI) are small droplets of silicate liquid trapped by minerals growing either with or from the melt [1]. Most MI in anatectic terranes appear partially or totally crystallized due to slow cooling at depth, and have been named “nanogranites” [2]. MI represent a new and powerful method to study anatexis, because they can give information about melt compositions at the source region of crustal granites, including concentrations of H₂O [3].

There are very few studies of nanogranites, and only one has reported the presence of MI along a prograde metamorphic sequence from metatexites to diatexites [4]. We present a new occurrence of nanogranites along the prograde metamorphic sequence of Jubrique, located on top of the Ronda peridotites (S Spain). Jubrique represents a complete though strongly thinned (~5 km) section of upper to middle-lower continental crust, ranging from carbonates and low-grade phyllites at the top to felsic Grt-bearing metatexites and granulites at the bottom and in contact with the peridotites.

MI show partially irregular to well facetted negative crystal shapes and occur in cores and rims of Grt porphyroblasts. They show a variable size, from ~5-10µm to several tens of µm in diameter; some of them reach up to ~200-300µm. Because of the large size, nanogranites at Jubrique have the potential to be remelted and analyzed by EMP but also by LA-ICP-MS. Nanogranites are composed of rare glass, daughter phases Qtz, Pl, Kfs, Bt and Ms, and solid inclusions of Ky and less frequently Gr, Hc, Rt, Ilm, Zrn, and Mnz. Ky was the main solid phase that favored the trapping of MI by poisoning crystal surfaces during Grt growth.

Previous studies concluded that anatexis in the granulites occurred in the Sil field during decompression and thinning. The presence of Ky+Rt within MI, and their occurrence in the high-P cores of Grt, indicate that partial melting in granulites and migmatites initiated at high P conditions, and that most Grt in these rocks crystallized in the presence of melt.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Study of Zsolnay building ceramics in aspect of deterioration by environmental factors

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The Zsolnay products are the one of the most famous Hungarian ceramics. The glazed building ceramics produced by the Zsolnay Factory were often applied to decorate the buildings, mainly around the turn of the 19th-20th century and since their outplacements the ceramics have suffered numerous environmental and human influences. Our purpose is to observe the alterations by environmental factors considering that these ceramics have never been studied in this aspect before. The studied objects were used on two buildings in Budapest. We have examined the major characteristics of the glaze and the ceramic body on two buildings in Budapest, the depositions on the surface of the glazed and the unglazed sides of some selected ceramics. Several types of Zsolnay ceramics were used as building materials on these buildings. We distinguished different kinds of damage, black deposition layer and alterations. Natural and artificial particles (e.g. carbonaceous and Fe-rich), spherules and a characteristic gypsum layer frequently cover the studied objects. Traces of biological activity (hyphaes) were also found and connected to these organic residues calcium-oxalate (weddelite) was identified. On some samples the glaze has started to weather and the lead leached from the thin surface layer of glaze by rainfall and, if this phenomenon continues for a long period, it will result in the deterioration of the whole glaze.

Trends in urban biogeochemistry at the Anthropocene

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As socio-natural sites [1], cities create a specific biogeochemistry [2], mainly because they attract huge amounts of materials concentrated in very small areas. This urban metabolism is the result of two intertwined phenomena: the natural processes on one hand, the technical ones on the other. Its study calls for an interdisciplinary approach as illustrated in [3]. In order to better characterise urban metabolism, we chose Paris urban area as a case study. By crossing historical methods and material/substance flow analysis, we were able to describe long term trends and changes. These results, together with other ones for other cities, allow to give a general insight into urban key issues in terms of biogeochemistry.

The very characteristic of cities is the externalisation of a great (and up to now growing) part of their metabolism. Cities were borne from a specialisation that made possible for some people to not produce their food and then to develop other activities in specific places – cities. This externalisation peacks with industrial revolution(s) with, for instance the partial externalisation of water cycle, the one of urban by-products transformation, etc. The shift of cities from sink (up to the end of the 19th century) to source of emission to air and water for substances like N or P is another characteristic of cities metabolism. This is due to changes in waste management and to the devalorisation of urban fertilisers (especially human manure) that occurred at the beginning of the 20th century together with the increase in fossil fuel consumption (for N).

As a result, urban metabolism goes far beyond the urban limits and cities can be considered as one of the main drivers of biogeochemical cycles, considering both their direct and indirect impacts on them. Today, one of the great challenges faced by urban managers and biogeochemists is the improvement of urban metabolism (its re-internalisation?), its transformation from a constraint to an asset – for the provision of nutrients, the reduction of urban heat island, etc.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Investigating instrumental mass bias in MC-ICP-MS using isotope ratio plasma profiles

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In multi-collector inductively-coupled-plasma mass spectrometry (MC-ICP-MS) heavy/light isotope ratios are fractionated to high values relative to the true value. Accurate and precise correction of this instrumental mass bias is a prerequisite for accurate MC-ICP-MS isotope ratio data. However, understanding of this phenomenon is limited.

As a step towards gaining insight into the processes involved in generating instrumental mass bias we have measured the variation of heavy/light isotope ratios as sampling depth in the plasma is varied. These axial plasma profiles were measured at ~250µm intervals over a sampling depth of ~3.5 mm. Each experiment consisted of 6 profiles sampled over the same sampling depth range but tuned at different sampling depths.

Pb and Mg were chosen as the analytes. These elements though very different in mass have similar first and second ionisation potentials, therefore any differences in heavy/light isotope ratios variation with sampling depth should be mass dependent. All profiles were curvilinear. For Pb the heavy/light isotope ratio (208Pb/206Pb) increased with decreasing sampling depth, whereas for Mg (25Mg/24Mg) it decreased. 208Pb/206Pb values on individual profiles varied by 0.56 – 0.70% of the average value measured on the profile and the magnitude of variation increased as the tuned sampling depth decreased. Variation in 25Mg/24Mg was much greater, 1.1 – 1.3% of the average value measured on each profile and increased dramatically to 7.1% for the profile tuned at the shallowest sampling depth. If only ratios measured at the tuned sampling depth on each profile are considered, the trends are reversed e.g. 208Pb/206Pb generally decreases with decreasing sampling depth.

These apparent variations in instrumental mass bias with sampling depth in the plasma result from a combination of processes occurring during transport of the analyte through the plasma (e.g. radial mass dependent dispersion of ions and atoms and ionisation potential effects) and additional mass dependent effects produced during sampling and transport through the interface. The contrast in apparent mass bias response between Mg and Pb allows us to speculate on the relative significance of plasma versus interface processes in producing the instrumental mass bias.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org

Subduction channel or fossil rifted margin? Serpentinite geochemistry of the Punta Rosa Unit, Western Alps

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The Punta Rosa unit (PR), now stacked in the Valaisan domain (Western Alps) preserves evidence of Mesozoic mantle exhumation at the seafloor, despite having undergone pervasive Alpine deformation/metamorphism. Serpentinites are overlain by slivers of continental basement or metasedimentary breccia and have been interpreted as an ocean-continent transition (OCT) based on structural data [1]. However, similar lithological associations throughout Alpine-type orogens are often interpreted as subduction-related “tectonic mélanges” [e.g., 2]. Here we present the first geochemical study of PR serpentinites to further test the interpretation of their tectonic setting.

Stable isotope and major and trace element compositions of PR serpentinites with varying distances from the contact with meta-sedimentary material were determined. δ18O, δ34S, and δD values range from +1.1 to +2.7‰, +7.0 to +8.5‰, and -50 to -73‰, respectively. δ37Cl values are some of the highest reported for serpentinites and increase towards the contact with the metasediments, indicating interaction with metasediments/alkaline oceanic crust during Alpine subduction/exhumation. O and H isotope data are consistent with low-T interaction with seawater (with partial resetting of H by meteoric fluids) or slab-derived fluids. Bulk serpentinite samples have high REE concentrations, compared to typical mid-ocean ridge serpentinites, with nearly flat to slightly convex up REE patterns (LaN/SmN = 0.38 – 0.62; LaN/YbN = 0.20 – 0.47; SmN/YbN = 0.41 – 0.89). These high REE concentrations are similar to those observed in OCTs (Iberia Abyssal Plain; Newfoundland) [3] and the Malenco and Platta peridotites (Switzerland), which are the type localities for preserved OCTs [4]. Serpentinite geochemistry supports stratigraphic and structural evidence for an abyssal origin of the PR serpentinites, providing a powerful tool to determine tectonic setting in poorly exposed/highly deformed metamorphic units.

Archean andesites as products of plume/crust interaction?

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A key line of evidence for Archean plate tectonics rests on the presence of andesites, the signature rock type of modern subduction zones. This study considers the petrogenesis of andesites from the 2.7 Ga East Yilgarn Craton (EYC) in Western Australia, a richly mineral-endowed terrane that has been a prime focus of debate between proponents of a uniformitarian, plate-tectonic driven interpretation, and advocates of an alternative plume-driven model. While EYC andesites have incompatible trace element characteristics similar to those of modern island arc andesites, they have unusually high Ni, Cr and MgO contents. This suggests the possibility that they contain a substantial mantle plume component. To test this hypothesis, we consider the major and trace element compositions of these rocks in relation to the entire assemblage of EYC volcanic rocks with ages between 2690 and 2710 Ma, including komatiites, plume-derived basalts and dominantly dacitic felsic rocks. The dacite component occurs as part of a bimodal association with simultaneously erupted komatiites, with characteristic TTG-like trace element chemistry, and chondritic to slightly depleted Nd and Hf isotopic characteristics. This component is interpreted as the partial melting product of underplated juvenile or near-juvenile mantle-derived mafic material. Numerical modelling of fractionation of plume-related tholeiitic basalts coupled with contamination by the TTG-like dacite component provides a good fit to all of the essential major and trace element characteristics of the EYC andesites, and is also consistent with the chondritic to slightly depleted Nd and Hf isotopic characteristics of the andesites[1]. Thus, a rock type previously taken as a key line of evidence for plate tectonic processes can be explained just as well by an alternative plume-driven mechanism, consistent with the overwhelming plume-derived character of basalts and komatiites across the entire craton[2]. This explains a paradox, noted in a number of papers, that apparently subduction-related rocks are interleaved with voluminous basaltic magmatism derived from 1000 km-scale plume-head arrival events. The problem is moot if Archean andesites are products of plume, not subduction zone, magmatism.


Isotopic tracing of ancient metal production using geological and mining archaeological research – Gaul mining from Limousin and Morvan (France). A case study

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The isotopic tracing from mines/ore bodies to archaeological materials (slags, metals, objects) constitutes a powerful tool in metal provenance studies. The progress of high resolution mass spectrometers (MC-ICP-MS) during the last decade currently facilitates accurate analyses of traditional and non-traditional isotopes, allowing thus precise and consequently more accurate interpretation [1]. Nevertheless, these high precision isotope analyses on ores are often carried out in an elusive way ignoring the geological approach as well as the mining archaeology background. The currently used lead isotope ores database is not completely relevant for the tracing of the ancient metals for several reasons: i) the isotopic composition of the analysed ores is usually not linked with their mineral paragenesis, and ii) the analysed ores are not those really exploited by the ancient miners. Furthermore, the ancient chaîne opératoire from ores to metal(s)/objects is not systematically considered [2].

Through an example of metal production in Gaul (France) during Protohistoric times, we demonstrate the importance of establishing a geochemical tracing based on geological and chronological/archaeological samples.

Our aim is to characterize the mining activity and the metal production at regional scale (Limousin and Morvan) and in a second stage to acquire the isotopic and trace element signature of the exploited ores and the produced metals (Au, Ag and Sn). This approach based on geological, mining archaeological and geochemical studies will refine the tracing of the metals at least for Limousin (5th to 1st centuries BC) and Morvan (2nd to 1st centuries BC) and will allow to obtain isotopic data bases needed for relevant metal provenance studies.

Acknowledgments: Research carried out in the frame of ANR MINEMET project (France).

Silica and germanium cycling in a coastal shelf environment: Insights from northern Gulf of Mexico
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The Ge/Si ratio recorded in sedimentary opal covaries with glacial-interglacial cycles as far back as the Mid-Miocene [1], demonstrating its potential as a proxy for Si cycling. However, there are multiple mechanisms potentially influencing the Ge/Si recorded. These include the intensity of terrestrial rock weathering, variations in the size of the diagenetic Ge sink, and biological fractionation by marine silicifiers.

We have measured Ge and Si concentrations in the water column and sediment pore waters in the Gulf of Mexico (GOM). Results indicate extensive fractionation, enriching the shelf surface water Ge/Si to 2.3 (all Ge/Si ratios are in µmol/mol), significantly higher than the main Si source - the Mississippi River (Ge/Si = 1.5). Preliminary box model calculations predict a fractionation factor of Rbiogenic silica/Rwater = 0.5-0.6, where R is Ge/Si ratio. GOM deep water (500-2100 m Ge/Si = 0.82-0.86) is also enriched relative to the published global ocean values (Ge/Si = 0.70-0.76). Porewater observations in coastal sediments (Ge/Si = 0.3-0.7) and modelling suggest that 10-30% of Ge is diagenetically sequestered into an unidentified (possibly iron-rich) authigenic precipitate.


Ferrian chromite formation in podiform chromitites from south-central Chile
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The metamorphic basement of the Coastal Cordillera in south-central Chile comprises two units with constrasting characteristics. The Eastern series is characterized by high T/low P conditions, whereas the Western Series represent high P/low T metamorphic conditions [1]. These units have been interpreted as an accretionary prism, where the Eastern series formed by frontal accretion and the Western series was produced by basal accretion [2]. The Western series comprises mainly metapsammopelitic rocks, metabasites and minor serpentinized ultramafic rocks. The serpentinite bodies are scattered within the Western series and show variable degrees of serpentinitization. Although most of these serpentinites have accessory chromian spinels, only in one locality podiform chromitites have been found. Here we present the chemical composition of these chromitites determined using electron microprobe analysis (EMPA) in order to provide some insights on the formation of ferritchromite as an alteration product of chromite.

Chromitites are highly brecciated with a matrix completely altered to Cr-rich chlorite. Chromite spinel grain cores are high-Al in content, whereas ferrian chromite (i.e., ferritchromite) is Fe3+ rich and usually formed along cracks and margins. The observed pattern of alteration is similar to that described for other locations [3] with volume reduction associated with dissolution of chromite and formation of porous chromite. Unaltered chromite cores show Cr# [Cr/(Cr + Al) atomic ratio] = 0.65-0.70, Mg# [Mg/(Mg + Fe2+) atomic ratio] = 0.50-0.70, and Fe3+/(Fe3+ + Fe2+) <0.15. The chemical composition of chromites evolved towards higher #Cr (0.75-0.95), lower #Mg (0.40-0.10), and higher #Fe (0.20-0.40). The observed trend is consistent with a reaction of chromite with olivine to produce chlorite. The alteration process is concomitant with mass loss and development of a porous texture in chromite.

Reconstructing past hydrology from annual cycles in trace elements in a Moroccan Stalagmite

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We present annually resolved trace element and stable isotope data from a laminated Mid-Holocene north Moroccan stalagmite. All reported analyses were performed on the same 200-μm micro-milled calcite samples, yielding an entirely inter-comparable dataset. In addition to δ18O, δ13C, Mg, Sr, Ba, U and P, we present the first measurements of Cd in speleothem carbonate. Recent cave-analogue experiments [1] demonstrate that Cd/Ca is highly sensitive to variation in the amount of calcite precipitated from solution, with high Cd/Ca particularly indicative of low degrees of prior calcite precipitation. We employ a multi-proxy approach, using Cd alongside other trace elements and stable isotopes to reconstruct changes in hydrology at this site.

With the exception of δ18O, highly distinct annual cycles occur in all reported proxies and correspond closely to changes in laminae colour. The observed annual cycle in Cd/Ca implies that % calcite precipitated is a major driver of annual trace element cycles in this sample. The agreement between the trace elements, laminae colour and δ13C agrees well with that expected in calcite precipitated in a site where rainfall is highly seasonal. Weaker correlations with δ18O reflect the more integrated nature of the information recorded by oxygen isotopes, indicating that some regional signal is being captured.

Despite differences in seasonal cave ventilation these observations show remarkable agreement with annual trace element cycles from a modern speleothem at St Michael’s Cave, Gibraltar [2], which lies 27 km northwest of our site. Such a parallel between sites gives confidence that trace element geochemistry can potentially be used for robust regional palaeoclimate reconstruction, and perhaps also for the careful extrapolation of monitoring studies between sites.


Ancient recycled nitrogen isotope signatures in Siberian xenoliths

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Siberian xenoliths display compelling evidence for a recycled crustal origin. In order to assess if nitrogen is also recycled in ancient subducted-oceanic crust we have measured N-isotopes (δ15N) and elemental (N2/Ar) ratios for a suite of peridotitic and eclogitic xenoliths (n=10) from two petrologically-distinct kimberlite pipes (i.e., Udachnaya and Obnazhennaya). Additionally, all samples have been well-characterized, mineralogically, petrographically, and for major and trace element chemistry.

Crustally-derived xenoliths (Gt, Cpx and Ol) of Siberia are believed to originally be derived from subducted oceanic crust which has since amalgamated to form the Siberian craton. The occurrence of non-mantle-like oxygen isotope signatures in Siberian xenoliths suggests that these lithologies are artifacts of partially-melted subducted ocean crust [1, 2]. Subsequently, this material was transported to Earth’s surface via kimberlitic volcanism. The age of Siberian xenoliths have been constrained to be within 2.7 - 3.1 Ga using Re-Os and Sm-Nd isotope dating techniques [3]. Mg#Gt ranges from 86 - 96, suggesting relatively primitive magmas. Major and trace element chemistry indicates that these samples have been subjected to varying degrees of metasomatism. Due to the antiquity of these particular xenoliths, they represent prime targets for N-isotopes, which have been previously suggested to show a secular variation throughout Earth history [4].

N-isotopes (δ15N) of Siberian xenoliths range from -0.7 to -10.8 % and are consistent with both upper mantle (MORB = -5 ± 2 ‰) and recycled contributions (modern sediments = +6 ± 2 ‰). N2/Ar values range from 32 to 178, spanning both atmospheric (84) and typical mantle values (84-164). Cpx mineral separates retained the most nitrogen gas. Notably, all Obnazhennaya samples display N-isotope values above the MORB range, indicating a larger contribution from a recycled component vs. Udachnaya samples, which span the MORB range. These results suggest xenoliths of different kimberlite pipes sample isotopically-distinct parts of the mantle, and may preserve varying mantle/crustal contributions throughout Earth history.


DOI:10.1180/minmag.2013.077.5.2

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Tracking Indian-type mantle at its western limit during the closure of Neo-Tethys and opening of the Indian Ocean

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Since the work of Mahoney et al. [1] on old west Indian Ocean and east Tethyan MORBs, we have known that Indian-type (DUPAL) mantle resided beneath at least parts of Neo-Tethys at the time of opening of the Indian Ocean. Furthermore, work on a ~350 Ma ophiolite from China [2] demonstrates that Indian-type mantle must have contributed, in some places, to MORB genesis during the formation of Paleo-Tethys. Together, this evidence suggests that Indian-type mantle has at least to some extent remained within the shallowmost asthenosphere during multiple Wilson cycles, over 100’s millions of years.

In the western Pacific the margins of the Indian-type mantle have been recognised and, in places, mapped adjacent to Pacific-type mantle [e.g. 3-5]. Detailed work along this boundary has shown that very little mixing has taken place, but what happened to the Indian-type mantle at its western limit during the diachronous closure of Neo-Tethys?

Using robust Hf-Nd isotopes on an extensive suite of MORB rocks from Neo-Tethyan ophiolites, extending from the Himalayas, through the Mediterranean and Europe, to earliest central Atlantic and proto Caribbean ocean crust, we assess where Indian-type mantle occurred beneath Neo-Tethys. Inferences from these results are then linked to 3D numerical spherical geodynamic models (run using mantle circulation code TERRA) and used to investigate models of how this isotopically distinct Indian-type mantle may have been preserved in the upper mantle during successive events of ocean closure and re-opening, with little apparent tendency to mix laterally.


Water contents of natural anatectic melts: constraints from NanoSIMS analysis of remelted nanogranites and glassy inclusions

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Formation, extraction and ascent of hydrous anatectic melts to upper crustal levels represent the most important mechanisms for the reworking of the Earth’s continental crust [1, 2]. In this scenario, the water content of melts is of prime importance in the formation and evolution of the continental crust and so far the experimental approach has been largely applied for obtaining constraints on the water content of anatectic melts.

The study of melt inclusions hosted in peritectic phases of partially melted rocks represents a recent, small-scale powerful approach to a better understanding of melting in the continental crust [e.g. 3-5]. Successful experimental rehomogenization of the inclusions to a glass allows the direct analysis of the natural anatectic melts produced in the source region of crustal magmas [5]. This approach provides the precise melt composition for the specific anatectic rock under study.

We report the results of NanoSIMS analyses on melt inclusions hosted in peritectic garnet of partially melted metasedimentary rocks. Data are discussed in order to i) combine information from classical petrology and melt inclusions, ii) compare them with previous estimations from experiments and thermodynamic calculations and iii) deal with new questions, such as the water content heterogeneities of natural anatectic melts in the source region.

Fate and impacts of nano-CeO$_2$ in an activated sludge bioreactor

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Widespread use of Engineered Nanomaterials (ENMs) in a myriad of consumer products and technologies has lead to release of ENMs to the environment. A likely first route of environmental exposure of ENMs is through the waste stream. Within wastewater treatment plants (WWTPs) ENMs undergo transport and transformation processes different from traditional organic contaminants. Understanding ENM-specific fate and transport is thus a critical void in current nanomaterial research.

In this study, we tracked the mobility and transformations of a common ENM, CeO$_2$ to determine realistic concentrations and the nature of the ENMs released from WWTPs in solid and effluent. An aerobic bioreactor seeded with sampled activated sludge was dosed with pristine and citrate coated CeO$_2$ chronically at environmentally relevant concentrations for a six week period. Two samples of CeO$_2$ were employed to observe the impact of surface chemistry on fate. During the lifetime of the reactor, affinity of the ENM for the solid versus liquid phase was measured and it was observed that > 90% of the added CeO$_2$ associated with the solid phase regardless of the surface coating. In addition, Ce speciation was monitored with XANES to explore the CeO$_2$ transformations. It was found that after 5 weeks in the reactor environment, strong reduction of the Ce(IV) in the ENM to Ce(III) occurred. Reduced Ce(III) was only measured in association with the solid phase indicating the key role of the microbial communities in promoting this reduction. In addition, it was seen that the citrate coating altered the kinetics of this reduction by preventing it until consumption of the coating by the bacteria. Determination of the interaction with the biomass and nature of the Ce(III) complexes is ongoing. Studies such as these can help inform the modeling community attempting to predict exposure and risk of ENMs released to the environment.

New interpretation of kinematics and morphogenesis of block structures of the Black Sea-central transcaucasian terrane

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Modern structure of the Black Sea-Central Transcaucasian Terrane is mainly conditioned both by meridional and latitudinal fault systems. They encompass different depth of the Earth's crust crystalline basement. They as a whole make a mosaic-block pattern. The analysis of lithofacies and thicknesses of sedimentary cover sometimes establishes their autonomous and inverse nature of development as well as differentiated kinematics. The research data enables to make the following conclusions: The Caucasian molasse depression (within the territory of Georgia) is divided into eastern and western subsiding zones by the Dzirula (crystalline basement) salient; they are also divided by faults into separate restricted blocks. Westwards and eastwards of the central uplift zone, along the faults is outlined a gradual "stepwise" submergence and tilting of blocks of the crystalline substrate. In the modern literature the analogous structures are known as the so called "tilt" blocks and kinematically they are related to tensile strains.

Thus, in contemporary structure of the pre-Alpine crystalline basement of the South Caucasian molasses depression (along the latitudinal profile) is marked the existence of tension structure mainly in condition of stepped-inclined blocks, which subsequently turn into the so-called listric faults. The appearance of this one is bound up, on the one hand, with uplift of the mantle masses in some parts of the region and on the other hand, with advance of the Arabian plate to the north and connected with them lateral squeezing out of masses both to the west and the east especially at the late-orogenic (collision) stage of development.
Effects of heating on the leaching of U-Th series radionuclides in a suite of natural minerals

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The differences in the extent of leaching (with 0.1 N HNO3 for ~25 days) and recoil of U-Th series radionuclides [U (234U), Th (230,234Th), Ra (224,226,228Ra), Pb (210,212Pb), 210Po, 228Ac and 222Rn] from a suite of natural minerals (zircon, monazite, thorite and cerite) were assessed at room temperature and after heating these minerals at 200 °C and 600°C. Our results indicate the following: i) The concentrations of U-Th series radionuclides in the leachate depend on the amount of the accumulated radiation dose in the minerals; ii) The amount of radionuclides leached from annealed (200°C or 600°C) minerals is lower by 3 orders of magnitude compared to unannealed minerals; and iii) The differences in the daughter/parent ratios of a number of pairs in the 238U and 232Th series (210Po/210Pb, 228Ac/228Ra, 234Th/238U, 212Pb/224Ra, 224Ra/228Th and 222Rn/226Ra) between the heated and heated minerals range over several orders of magnitude.

This study provides insight on the location of 238U and 232Th and possibly their daughter products in mineral grains (in particular, if they are located in grain boundaries), the effects of track density on the leaching of U-Th series radionuclides from mineral grains, the effects of the internal radiation damage on the escape of radon and the leaching of other non-gaseous daughter products in the U-Th series. This study has implications on the assessment of the performance of nuclear wasteforms in groundwater environment. This study has also bearing on the mobility of U-Th series radionuclides in rocks/minerals that are in contact with erupting magma.

We will present possible mechanisms for the differences in the extent of leaching of radionuclides between the heated and unheated minerals in our presentation.

Internal Lu-Hf isotope systematics of the quenched angrite D’Orbigny and two plutonic angrites

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The long-lived radioactive decay of 176Lu to 176Hf potentially provides a precise and disturbance-resistant chronometer for dating early Solar System processes. However, some meteorites (e.g., the quenched angrite Sah 99555 [1]) show excess 176Hf [1-3], resulting in Lu-Hf dates significantly older than the Solar System. One possible explanation for this is that irradiation in the early Solar System produced the short-lived isomer 176mLu (t1/2 = 3.7 hr) and thus accelerated the 176Lu-decay [4-5].

In contrast to the results of Sanborn et al. [6], we found excess 176Hf in the quenched angrite D’Orbigny and the plutonic angrite NWA 4801. Our internal Lu-Hf isochrons yield dates of 4760 ± 64 Ma for D’Orbigny (8 fractions) and 4635 ±19 Ma for NWA 4801 (10 fractions). The initial 176Hf/177Hf values are 0.279736 (37) and 0.279788 (89), respectively, which are in the same range as the CHUR values of [7-8] back-calculated to 4567 Ma, and 3-6 ！-units higher than the initial Hf isotope composition of the Solar System suggested by Bizzarro et al. [1].

Our new data do not preclude irradiation on the angrite parent body as a possible cause for the old apparent ages. However, not all Lu-Hf dates are too old: our 8-point Lu-Hf isochron for the plutonic angrite NWA 4590 yields 4580 ±46 Ma, which is in agreement with the Pb-Pb age reported by [9-10]. Its initial 176Hf/177Hf value of 0.279794 (16) agrees with the CHUR values of [7-8] back-calculated to 4567 Ma, and 3-6 ！-units higher than the initial Hf isotope composition of the Solar System suggested by Bizzarro et al. [1].

We will present possible mechanisms for the differences in the extent of leaching of radionuclides between the heated and unheated minerals in our presentation.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Zeolites and mafic phyllosilicates in Livingston Island, Antarctica

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The present work is a report on the geochemistry and petrology of the very low-grade alteration minerals developed in the volcanic successions from Punta Hannah (PH) and Shirreff Cape (SC), Livingston Island, Antarctica. The outcrops consist of andesitic-basaltic rocks from volcanic successions assigned to the Upper Cretaceous [1]. These rocks are one of the most extensive volcanic exposures in the South Shetland Islands. The alteration minerals occur in amygdules, veins, veinlets, groundmass, or patches. This replacement of the phenocrysts can be partial, affecting the crystal edges and fractures or total. Primary plagioclases have been strongly altered to albite, zeolites and calcite, and clinopyroxenes to mafic phyllosilicates and celadonite.

Petrographic, XRD and EMP analyses show the occurrence of the zeolites: laumontite, stilbite, faujasite and heulandite in PH, and natrolite and analcime in SC. Mafic phyllosilicates correspond to interstratifications between chlorite and triotchahedral smectite. Chlorite layer percentages range between 57% and 84%, and display diabantite compositions [2]. Equilibrium temperatures of mafic phyllosilicates from PH, calculated using two geothermometers [3, 4], range between 160 and 190°C for those with chlorite layer percentages above 75%. This range is in agreement with temperature estimates for zeolites of 150-230°C. Zeolites from SC suggest temperatures below 150°C. The characteristics of these rock successions indicate a Ca-Na remobilization in the light of albitionization and the widespread occurrence of Ca-rich zeolites. Hydrothermalism and burial processes would account for the genesis of the secondary minerals.

Project Anillo CONICYT ACT 105 financed the research.

FreeGs thermodynamic database project: implementation, lessons, and future?

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Increasing demand in reactive-transport modelling for the purposes of CO2 sequestration, use of geothermal energy, and nuclear waste disposal requires ready access to standardised thermodynamic data. These must be adopted for multiple formats for ever increasing number of modelling applications.

FreeGs [1, 2] is a web-enabled database developed at Geoscience Australia by the Predictive mineral discovery Cooperative Research Centre (2001-2007). It was intended as a unified Australian hub of thermodynamic data for geochemical modelling for economic geologists. The database was complemented by integrated software to calculate thermodynamic properties of species and chemical reactions at elevated temperatures and pressures. The end users had put a critical emphasis on the following decisive features:

• High end-user usability in an interactive mode
• Transparency of the compiled data
• Extendibility (data formats & incorporated models)
• Options for remote access and maintenance

In the interactive mode, FreeGs readily facilitates (1) comparison of TD data compiled from different sources, (2) their model presentation via alternative algorithms (equations of state), and, (3) output of data in alternative formats (e.g., $\Delta g(T,P) \text{ vs } \log K_r(T,P)$).

Despite these features and a friendly web GUI, practical usage of the database system by the scientific community was rather limited. As we see it, the development of a human interface and integration with calculation algorithms were over-emphasised at the expense of the implementation of the data delivery web service. That hindered efficient access to data by external parties and created avoidable development and maintenance overheads.

The future of a similar database will lie in the realm of a database located on a cloud server with (1) HTML access (“find and read”) for simple and infrequent interactions, and (2) web service for the delivery of plain standardised data that can be further processed by users applications as needed.


DOI:10.1180/minmag.2013.077.5.2

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A new strategy for identifying shales with high gas retention using noble gas, nitrogen and carbon

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Noble gases have been used to distinguish between hydrocarbon maturities, and evaluate the fracture network in a shale [1]. Carbon and nitrogen isotopic ratios, and noble gases, have the potential to identify the origin of shale gas. A combined study using all three simultaneously can strengthen previous applications, and have the potential of further utilizations. But such studies on shale gas cuttings are non-existent.

The preferential adsorption of Xe and Kr is higher for kerogen than shales [2]. So, distinct fractionation pattern should set apart organic-rich shales. In conjunction with carbon and nitrogen isotopes, C/N and N/Ar ratios, they can provide useful insights on the type of sedimentary organic matter. A combination of stepwise combustion and vacuum crushing can be used to decouple the free and bound gases.

Acknowledgement: We thank the BG Group for a Research Grant 2013-17


A new analytical protocol for high precision EPMA of olivine

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Composition of olivine provides critical information on the composition and origin of primary mantle derived melts and their sources. Especially informative are minor and trace elements Ni, Mn, Ca, Al, Cr, Co, Ti, Zn, P, Na [1, 2], which being in the concentration range over 10 ppm are assessable by EPMA.

Long counting times (up to 300 sec) on WDS at high beam current (300 nA) reported in [1] yield precision of individual analysis around 30 ppm (2 standard errors) for Ni, Mn, Ca, Al, Cr and 300 ppm for Fo content of olivine. Here we report 2-3 fold improvement of EPMA precision for larger range of trace elements in olivine (Ni, Mn, Ca, Al, Cr, Co, Ti, Zn, P, Na).

The analytical protocol built up on brand new JEOL JXA 8230 EPMA in ISTerre, UJF, Grenoble, France. Facility has tungsten source gun, is equipped by five WDS and one SDD EDS and placed in the environment with controlled temperature (22±0.3 degrees C) and humidity (50±3%).

The analytical conditions are the following: acceleration voltage 25kV, 900 nA beam current, WDS recording for trace elements (Ni, Mn, Ca, Al, Cr, Co, Ti, Zn, P, Na) and EDS recording for Si, Mg, Fe, total counting time 12 minutes, ZAF correction. Instrumental drift during analytical sessions is monitored by repeated measurements of olivine standards. For trace elements this protocol yields detection limits from 3 to 10 ppm and average precision of individual analysis of 10 ppm (2 standard errors). For Fo of olivine precision is 300 ppm (2 standard errors).

Comparison of EPMA and LA ICP-MS data for the large range of olivine compositions suggests that accuracy of EPMA is similar to precision noted above. For elements with concentration over 100 ppm the obtained EPMA precision and accuracy are better than these of LA ICP-MS. For the concentration of elements between 50-100 ppm both methods show similar precision and accuracy; and for concentration between 10-50 ppm LA ICP-MS yields better precision and accuracy. Spatial resolution of EPMA, however, is significantly better: 3-5 micrometres compared to 30-50 for LA ICP-MS. This makes our new EPMA protocol of great advantage for measurement of zoned or small olivine grains.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Delineation of groundwater zones using weighted overlay analysis of hydrochemical and multiple isotopic data, Ulaanbaatar, Mongola

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The water demand in Ulaanbaatar (UB), the capital of Mongolia, is quickly increasing due to significant population growth. Municipal water supply in UB depends solely on groundwater withdrawn from alluvial aquifer that is developed along and near the Tuul River. To overall understand the status of groundwater in UB, we performed a hydrochemical and environmental isotopic survey. Concentrations of cations and anions, δ13C of dissolved inorganic carbon, δ15N and δ18O of nitrate, and δ34S and δ18O of sulphate were analysed. Three major hydrochemical types of groundwater occur in UB: 1) Ca-HCO3 type, 2) Ca(-Mg)-HCO3 type, and 3) Ca(-Na)-Cl(-NO3) type. Types 1 and 2 mainly occur in forest and grassland areas at outskirts of UB and represent the natural water chemistry without anthropogenic contamination. Type 3 occurs predominantly in urbanized areas and is characterized by increased concentrations of TDS, Cl+NO3 (and NO2)+SO4 due to significant contamination. The δ15N and δ18O values of nitrate in type 3 groundwater indicate the main source of contamination from latrines (manure) and sewage. To delineate several groundwater zones under contamination risks, we conducted digital image processing techniques of remote sensing and GIS. Then, multi thematic maps on lithology, slope, land-use, lineament, drainage, soil and rainfall were integrated in a raster based GIS (i.e., weighted overlay analysis) to identify the weighted factors of groundwater contamination and to classify and map the groundwater zones as very poor, poor, good, and very good in relation to contamination susceptibility. The results of this study will be helpful for planning schemes for sustainable groundwater management in UB.

Raman spectroscopy and powder diffraction study of synthetic Coffinite (USiO4) at high pressures

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Coffinite, USiO4, can form under reducing conditions from UO2 in contact with silica-rich waters (Langmuir’s criterion) [1]. Spent nuclear fuel (SNF) consists to > 90% of UO2, therefore the safety assessment for a final repository in deep geological formation will benefit greatly if coffinite is taken into account as a potential secondary phase. While high pressures are not of specific relevance for a final repository for SNF, its structural behaviour at high pressures is of general interest to understand the phase stabilities and to benchmark model calculations. The high pressure behaviour of coffinite has been studied before on natural and synthetic samples [2,3]. A pressure-induced irreversible phase transformation from the zircon- to the scheelite-type structure was found at about 15 GPa using an alcohol-water mixture as a pressure medium [3].

Here, synthetic coffinite was studied under high pressure conditions in the diamond anvil cell with neon as quasi-hydrostatic pressure medium up to pressures of 35 GPa. The samples are free of impurities of UO2, as characterized by XRD and HRTEM. Powder diffraction experiments with synchrotron radiation indicate a pressure-induced phase transformation at 18-20 GPa. In contrast to the earlier high pressure study [3], this transformation is reversible on pressure release and no UO2 is formed during the process. A detailed data analysis is currently in progress.

Raman spectra were obtained up to a pressure of 18 GPa. Further measurements at higher pressures are on-going.

Financial support from the German Federal Ministry of Education and Research (BMBF) under grants 02NUK019C and 02NUK019E is gratefully acknowledged.

[3] Zhang et al. (2009), Am. Min. 94, 916-920

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Oxygen and hydrogen stable isotopes in Alpine waters and fine-grained soils near Saas Fee, Switzerland

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Samples of soil and surface water were collected along a transect of 30 km with 1600 m of difference in altitude in the valleys of Saas Fee and Visp in the Swiss Alps. Mineralogical, chemical, and isotopic (O and H) compositions were measured to study the water-rock interactions, clay mineral formation, and the influence of altitude on the isotopic composition of soils during weathering of the parent rock, in order to draw conclusions for the usability of hydrous minerals derived from alpine soils for paleoelevation studies.

Waters have a range of \( \delta^{18}O \) and \( \delta^D \) values typical of those for precipitation and glacial melt water, decreasing with altitude of the catchments. The major dissolved ions characterize the composition of the substrate lithologies by elevated contents of Ca, sulphate, K, and Mg ions. This is also the case for the mineralogical composition of the soils that corresponds to the occurrence of ophiolitic material in higher elevations and granitic gneisses and schists in lower regions. While phyllosilicates from early-stage weathering and transformation of illite and chlorite to interstratified minerals (vermiculite, illite-vermiculite, chlorite-vermiculite and illite-smectite) are present, their abundance is relatively low. The isotopic composition of the fine earth fraction and the \(< 2 \mu m\) clay component in the soil was in average identical, and corresponds to the range of values of the host rock material. This suggests that the present climate and this environment do not allow for the neoformation of larger quantities of clay minerals in contact with ambient water.

Pore scale visualization of chemical gradients at biogeochemical interfaces using micromodels and Raman microspectroscopy

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Biogeochemical interfaces (BGI) are controlling the fate of organic chemicals at the interface between the terrestrial and the aquatic environment. BGI are highly dynamic in the spatial and temporal domain. One of the key features of BGI is their limited temporal and spatial accessibility which is hard to imitate in conventional laboratory test designs.

Processes at BGI can be visualized and quantified using microfluidic structures mimicking the pore topology of the soil, so called micromodels. In combination with Raman microspectroscopy chemical information can be retrieved from a micromodel experiment with a spatial resolution on the order of 1 \( \mu m^2 \) and a temporal resolution in the s-range. To increase the sensitivity, silver nanoparticles have been added to the water phase flowing through the micromodel to make use of the amplifying surface-enhanced Raman effect. Currently chemical gradients of moderately lipophilic substances have been acquired with a limit of detection of \( 10^{-8} \) mol/L. Challenges to overcome include the interactions between silver nanoparticles and target analytes which might alter the mass transfer rates, and the settling of nanoparticles in the channel.

As high resolution acquisition comes with a limited field-of-view (FoV) and, e.g., the growth of a biofilm outside of the FoV alters the flow pattern, the flow velocity has to be monitored using fluorescent latex beads and single particle tracking. For a fast measurement of well-defined variables, like the pH-value or the oxygen concentration, thin film polymers with encapsulated sensor dyes are chosen.

When looking at microbial growth in porous media, not only the development of a biofilm changes the flow paths and the accessibility to the microbes, but also the development of locally confined gas bubbles, as with \( P. \) denitrificans. Here, the growth rate is correlated with bacterial activity and the results indicate different bacterial densities in pore bodies and pore throats.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Diverse hydrothermal venting at the Jan Mayen vent fields, AMOR

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The basalt-hosted Jan Mayen vent fields (JMVF) are located at 71° N on the southern end of the ultra-slow spreading Mohns Ridge (AMOR). Over the past few years, scientific cruises have repeatedly visited and extensively sampled these vent fields. Researchers have identified several types of hydrothermal venting and have noted significant differences in hydrothermal fluid compositions within relatively short distances. The types of venting range from focused high-temperature fluid venting from numerous chimney structures, to low-temperature diffuse fluid flow areas. In addition free gas bubbles were observed being released from the seafloor. The chemical composition of the high-temperature endmember vent fluids is primarily characterized by high concentrations of carbon dioxide together with low hydrogen and methane concentrations. Fluids from the diffuse flow areas are characterized by an increased concentration of methane, which is strongly reflected in the hydrothermal plume observed above these diffuse systems. High concentrations of dissolved methane together with low concentrations of dissolved hydrogen were measured in the water column close to the seafloor for the diffuse flow hydrothermal plume, while high hydrogen/low methane concentrations were found in the high-rising non-buoyant plume. The main constituent of the gas bubbles, however, was carbon dioxide. In addition, at 560 m water depth along the flank of a high-temperature venting chimney, formations of gas hydrate were observed. A few tens of meters away, a ridge segment with several small chimneys with a flame-like discharge was observed, suggesting subcritical phase separation through boiling at relatively low pressures. Here we present a study on the diverse geochemical fluid and gas characteristics of the Jan Mayen hydrothermal systems located on the ultra-slow spreading Arctic Mid-Ocean Ridge and compare the results with the fluid composition of other mid-ocean ridge hydrothermal systems.

The SwissSIMS ion probe facility

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A new ion probe laboratory, housing a CAMECA IMS 1280-HR has been established at the University of Lausanne, Switzerland in the Institute of Earth Sciences. The SIMS facility was obtained through funding from the Swiss National Science foundation, the universities of Bern, Geneva, Lausanne, and the ETHZ. It is organized as a Swiss National Facility, with a scientific steering committee. The instrument was installed in the second half of 2012, and it passed specification late 2012. The NanoSIMS facility of the EPFL under the direction of Dr. Anders Meibom is housed in the same building. The combination of facilities offers the users a unique opportunity for in situ surface analysis.

We will focus on basic and applied research in all domains of earth science. The IMS 1280-HR is equipped with high-density cesium and oxygen primary ion sources, 5 interchangeable electron-multiplier spectrometers (EMS) or Faraday cup and 2 fixed Faraday cups for multi-collection and one electron multiplier and two Faraday cups for mono-collection. The magnetic sector is stabilized with a Hall probe to improve reproducibility of isotopic ratios; transmission is optimized for IMS sensitivity.

So far we have tested and adapted existing methods on using NIST or MPI-DING standards and we improved existing method for Cl isotope measurements [1]. We are currently developing and establishing various carbonate standards for O and C isotopes, in house quartz standards for O and Si isotopes, as well as standards for oxygen isotopic composition for olivine, titanite, biotite for O isotopes. We are now ready to start the first scientific projects.

[1] Bouvier & Baumgartner, Session 201, Golschmidt 2013
Geochemical mapping in urban area of an old mercury mining town (Idrija, Slovenia)

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Detailed soil geochemical survey tackles the urban area of Idrija, which is the oldest mining town in Slovenia with about 7000 population. Strong legacy of 500 years of mercury mining and ore processing in Idrija have resulted in widespread contamination. Environmental impacts on a regional scale caused by atmospheric emissions from the Idrija ore roasting plant were established in investigations of mercury spatial distribution in soil on regional scale [1, 2].

This study is part of the URGE project (Urban Geochemistry) and brings into focus urban area of Idrija town. Soil was systematically sampled (45 sampling sites) in 4 km² of Idrija urban area. Two soil horizons (0-10 cm and 10-20 cm) were sampled in order to distinguish between different metal sources. Samples were prepared and analysed according to URGE project. A sampling model grid was developed for collection of 9 soil samples per km². Due to higher population density, the density of samples was increased in the town centre. Contents of potential harmful elements were determined using aqua regia digestion. As expected, Hg contents were extremely elevated and ranged from 8 to 1210 mg/kg with a median of 50 mg/kg for lower soil horizon and from 7 to 1550 mg/kg with a median of 60 mg/kg for upper soil horizon. Spatial distribution analysis shows that higher contents appear along river banks, where ore residues were dumped in the past and in the part of the studied area, where soils overly rocks containing mercury ore. Other potential harmful elements didn't show critical elevations and according to legislation, so the study was further directed into analysis of mercury species and their water-soluble and bio-accessible contents.
Precise U-Pb (ID-TIMS) and SHRIMP ages on single zircon for Achaean TTG rocks on Baltic Shield

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Voche-Lambina polygon lies on the boundary between Belomorian mobile block and Central –Kola domain (Morozova et al., 2011). New neoarhaean U-Pb data on single zircon from TTG of international polygon named of the Voche-Lambina yielded 3158.2±8.2, which are situated on Central-Kola block in the Baltic Shield. Zircon are characterized by low concentration U and Pb, low U/Th ratio with 0.2. REE diagrams of grey gneisses reflect high fractionation La/Yb>30, enriched by light REE and depleted by heavy Yb<0.6 ppm. Model Sm-Ng ages on the rocks have protolith from with the ages 3.4 to 3.2 Ga, positive εNd from +1.29 to +3.3, ISr equals 0.702. Precise age of amphibolites metamorphism has been dated on single zircon with 2704.3±5.9 Ma. In the frame of the Central-Kola domain there is an Ingosersky TTG complex. Firstly U-Pb dating on single zircon from Bt-gneisses reflects 3149±49 Ma. Metamorphic alterations were in 2725.2±2.5 Ma and connected with origin of Amf-Bt gneisses and 2733.6±6.6 with Bt-Amf gneisses. (NItkina et al., 2012). Achaean gneisses in Monchegorsk region were firstly dated in the Central-Kola domain and near Murmansk. Single zircon from gneisses in Monchegorsk region which are the basement for Paleoproterozoic PGE layered intrusions with U-Pb ages on zircon and baddeleyite from 2.4- to 2.5 Ga (Bayanova et al., 2009) has 3.16 Ga and single zircon with 2776±3 Ma is considered as amphibolites metamorphism. New U-Pb (ID-TIMS) data on single zircon from high alumina gneisses near Murmansk in the Central-Kola domain gave 3.17 Ga, core from these zircon population has the age 3695±5 Ma by SHRIMP. Time of amphibolites metamorphism was dated with 2753±3 Ma. Therefore based on the new data on single zircon from TTG and gneisses from Central-Kola domain leads to the long history of continental crust origin in the Baltic Shield from 3.16 to 3.7 Ga.

We thank to D. Wasserburg for 205 Pb artificial spike, J. Ludden for 91500 and Temora standards, F. Corfu, V. Todt and U. Poller for assistance in the establishing of the U-Pb method for single zircon and baddeleyite grains. The study is contributed and supported by IGCP 599 and Department of Earth Sciences RAS, program 4.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org

Improvements of the coherent and precise ice core dating tool Datice: new data and parameterization

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Recently, we published the new ice core reference chronology AICC2012 common for 5 ice cores (EDC, EDML, Vostok, TALDICE and NorthGRIP) back to 800 ka (thousand of years before 1950) [1, 2]. To construct this optimized chronology we used the “Datice” Bayesian tool [3], using a background chronology and data constraints (absolute and orbital age markers, stratigraphic links between the ice cores) for both the ice and gas phases.

One of the limitations of AICC2012 was the lack of a good characterization of variance associated with the thinning background scenario respecting the deformation history. We thus propose a new definition of this variance using numerous data of microstructure and fabric for the EDC ice core [4].

A second limitation of AICC2012 was the lack of orbital constraints on the long EDC ice core. We present a new high-resolution record of δ18Oatm and 18O 2/N2 between 100- 800 ka obtained on EDC ice of high quality exempt of gas loss. Together with the complete record of air content [5], another orbital dating tool, we provide an important step for improving the reference ice core chronology for Antarctic ice cores.

Mantle xenoliths preserve invaluable information on chemical and thermal events in the earth’s mantle and on the ages and rates of such events. The presence of Fe-Ti oxides such as ilmenite or armalcolite in areas affected by mantle metasomatism, for example, could constrain the oxidation state of the metasomatic event and provide information about the metasomatic agent(s). Here we focus on lherzolite- and clinopyroxenite-rich xenoliths from Cima Dome (California) and Chino Valley (Arizona), their unusual mineral assemblages, and their formation.

Fe-Ti minerals identified in the selected xenoliths include ilmenite and ilmenite. In the Chino Valley clinopyroxenite, Nb-rich and Nb-free rutile both occur, either included in or included by ilmenite. Moreover, ilmenite is initially replaced by Fe-oxide + kassite (a rare hydrous Ca-Ti oxide). Both ilmenite and rutile are rimmed by titanite. These successions imply a change from Fe-Ti to Ca-rich silicate metasomatic agents percolating through the host rock. In the amphibole-bearing lherzolite from Cima Dome, Ti-rich pargasite is surrounded by glass-1, spinel, plagioclase, clinopyroxene, olivine and armalcolite. The latter is entrained within the glass pocket and has a skeletal crystal shape suggesting rapid growth at high pressures ~1.0 GPa and low oxygen fugacity at mantle depths. The presence of glass-1 is associated with rapid melting and breakdown of pargasite to Ol+Cpx+Spl+Gl-1 en route to the surface. Glass-2 is observed along grain boundaries of pyroxenes and olivine, however is Si-enriched and depleted in Ca, Mg, Al, Ti compared to glass-1. Both samples suggest extended multi-stage histories involving partial melting to form primary minerals, a period of metasomatic alteration, and a short timescale of decompression upon eruption.

Storage of Initially Organic Nitrogen in Silicate Minerals and Volcanic Glasses

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We are investigating pathways by which initially organic N can be incorporated and stored in silicate minerals and glasses, focusing on phases other than the clays and micas, the latter known to house N as NH4+. Despite its volatility, N is surprisingly compatible in various silicates, largely as NH4+, but also as molecular N2 in microporous phases (e.g., beryl, cordierite, zeolites, melanoophlogite). These species can provide a record of ancient organic processes.

Along relatively warm prograde P-T paths, a significant fraction of the organic, mica-bound N in metasedimentary rocks can be lost at lower grades, due to partitioning into H2O-rich fluids generated by breakdown of layer silicates such as chlorite. This N loss could affect the degree to which ancient (e.g., Archean) low-grade suites can be used to extract paleo-environmental information. However, at higher grades, the remaining N is retained to a surprising degree, even in rocks that experience partial melting, in phases such as K-feldspar and cordierite. Thus uptake and long-term storage of atmospheric/organic N in early-formed continental crust is possible (Goldblatt et al., 2006). Δ15N values for coexisting cyclosilicates (N2) and micas (NH4+) in some pegmatites and metasedimentary rocks indicate preservation of N isotope fractionations like those predicted by theoretical studies.

Incorporation of N with organic δ15N in seafloor basalts can result in a seafloor N budget rivalling that in overlying sediments, strongly influencing the N subduction budget (Li et al., 2007). Our work on palagonitized volcanic glasses on the modern seafloor and in Mesozoic basalts, some of the glasses bearing microbial ichnofossils, demonstrates this uptake and that analyses of such glasses could be useful in the search for signs of ancient life on Mars. Low-grade metasalts in the Aabitibi Complex (2.7 Ga) contain small amounts of N, now in mica, with organic δ15N that could reflect Archean seafloor incorporation of sedimentary/organic N, likely via a pore fluid. Melanoophlogite, a silica clathrate found in low-T hydrothermal settings, contains up to 1700 ppm of N2 also with organic δ15N. Our ongoing work considers the extent to which such phases can store N without isotopic change for geologically significant time periods.
Composition of the oceanic crust: where have all the noble metals gone?

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It has been speculated that the low noble metal abundances of many evolved MORBs may reflect sulfide fractionation, either during melting, or, as a consequence of fractional crystallization in the oceanic crust [e.g., 1].

The depletion of incompatible noble metals and Re in lherzolitic fractional melting residues from the depleted mantle [2] can be used to estimate bulk peridotite-silicate melt partition coefficients for these elements at the specific P-T-fO2 conditions of melt extraction (DRe=0.7, DAu=0.12, Dpd=0.08). The data for Re are in good agreement with bulk partition coefficients calculated from experimental data at suitable upper mantle fO2. Calculated abundances of these elements in primitive melts at 5-10 % melting are 10 ppb for Pd, 10 to 6 ppb for Au, and 2 to 1 ppb for Re. This contrasts with typical abundances in MORB of 0.05-2 ppb Pd and 0.1-3 ppb Au, whereas Re shows good agreement [e.g., 1,3,4].

Because partial melting of depleted mantle lherzolite cannot explain noble metal abundances in “primitive” MORBs, fractional crystallization in the crust is commonly invoked [1,3]. New data for the PGE+Re in different lithologies of the lower oceanic crust at hole 735B (crust formed by very slow spreading at the SW Indian ridge), indicate even lower abundances of Pd, Au and Re than in many MORBs. Clearly, the main site of fractionation of the PGE must be deeper than the drilled section. Recent data from lower crust of the Wadi Tayin section of the Oman ophiolite suggests significantly higher PGE abundances in fast spreading oceanic crust [5]. However, even these higher abundances fall short of expected concentrations in the oceanic crust. We conclude from this that most of the noble metal fractionation in MORB magma likely occurs during magma transport in the uppermost mantle. Dunites and harzburgites from the mantle section of the Oman ophiolite are strongly enriched in Pt, Pd and Re, thus providing hints for such fractionation processes [6,7].


Thermal conductivity of \((\text{Mg,Fe})\text{O}\) from ambient to deep mantle conditions

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The thermal conductivity \(\kappa\) is one important physical property that controls the structure and the dynamics of the Earth's mantle [1,2]. Furthermore, \(\kappa\) influences the heat flux at the core-mantle-boundary and thus the generation of the Earth's magnetic field [3]. In spite of its significance, this parameter is insufficiently constrained due to the great technical challenges to measure thermal transport properties at pressure and temperature conditions relevant for the lower mantle. Here, we use an alternative approach and predict the thermal conductivity of model \((\text{Mg,Fe})\text{O}\) by equilibrium molecular dynamics simulations. We first investigate the effect of isostructure disorder on \(\kappa\) in pure \(\text{MgO}\) with natural isotopic composition by randomly distributing the three most abundant \(\text{Mg}\) isotopes in the simulation cell. At ambient conditions we find that earlier simulations of Haigis et al. [5], which used an average isotope mass for all \(\text{Mg}\) ions, overestimate the thermal conductivity by about 32%. This overestimation is comparable to the predicted 46% from phonon lifetime calculations [4]. With rising temperature, the influence of isostructure disorder on \(\kappa\) decreases and becomes almost insignificant at deep mantle conditions. Next, we analyse how the substitution of 10% or 20% of \(\text{Mg}\) by \(\text{Fe}\) masses affects \(\kappa\). Due to the larger mass difference between \(\text{Fe}\) and \(\text{Mg}\) ions compared to that between \(\text{Mg}\) isotopes, the reduction is now much larger at ambient conditions and still relevant at pressures and temperatures of the lower mantle. Combining our new results with those of Manthilake et al. for \((\text{Mg,Fe})\text{SiO}_3\) perovskite [6], an aggregate mantle of 20% \((\text{Mg}_{0.80}\text{Fe}_{0.20})\text{O}\) and 80% \((\text{Mg}_{0.97}\text{Fe}_{0.03})\text{SiO}_3\) perovskite has a thermal conductivity of 10±2 W/(m K) at 3000 K and 138 GPa.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Component specific Hf-W dating of Allende and Vigarano CV3 chondrites

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The formation of chondrules, matrix and other components of chondrites is not yet fully understood. Knowing their relative formation ages and genetic relationships can provide crucial information on their formation conditions. Short lived radionuclides can provide new insights into the chronology of the formation of early solar system materials. In the past, the 26Al-26Mg system has been mainly used for this purpose, but recently the 182Hf-182W system emerged as a promising tool to date chondrule formation. Thus, components of chondrites that never underwent high temperature metamorphism, like CV3 chondrites, are well suited candidates for Hf-W investigations. Earlier studies of Allende chondrules with the Al-Mg und Pb-Pb systems indicate that they formed up to 3.2 Ma after CAI formation1-4.

We prepared 23 Allende and 13 Vigarano separates for Hf and W isotope measurements, covering both reduced and oxidized CV chondrites. These include pure handpicked chondrule and matrix fractions as well as magnetic separates and bulk aliquots. The separates all define isochrons which indicates a contemporaneous formation of all components. The ages defined by the isochrons suggest formation of Allende and Vigarano components within 3 Ma after CAI formation.

Notably, W and Hf concentrations in chondrule and matrix fractions from Allende and Vigarano vary considerably. Chondrules from Allende exhibit high Hf/W ratios (2.5 to 3.0), whereas matrix and strong magnetic fractions exhibit low Hf/W ratios (0.5 to 0.9). Unlike in Allende, Vigarano contains chondrules with extremely low Hf/W ratios. As suggested from petrological observations, these low ratios can be attributed to the presence of metal inclusions within the reduced Vigarano chondrules.


Actinide redox processes on iron sulfides: an electrochemical, microscopic, and computational approach

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Little is known about the reaction mechanism of actinyl complexes on mineral surfaces, i.e. the role of the redox potential, the nature of the reductant, the importance of minerals in terms of providing catalytic surfaces, the role of anions in solution that polarize a mineral surface to promote or inhibit electron transfer, and the activated states that may slow down the kinetics of the redox process.

In order to resolve these, electrochemical studies using a micropowder electrode technique were performed in combination with a quantum-mechanical and microscopic (AFM) approach. The electrochemical approach allows us to determine the specific redox potential of actinide reduction on a given mineral surface. For example, uranyl reduction takes place at -0.22 V on hematite, -0.17 V on magnetite, and at -0.14 V on pyrite. Further electrochemistry experiments were performed on machinawite, in order to be able to compare these with quantum-mechanical calculations on the thermodynamics, charge and spin transfer, and electrochemical potential for reduction and oxidation to occur. The calculations show that the energy gain of the co-adsorption of hydroquinone (as an analogue for microbial reduction) and uranyl is on the order of 0.5 eV (≈50 kJ/mol) as compared to the separate adsorption of uranyl and hydroquinone. Similar co-adsorption on FeS (mackinawite) reveals that Fe(II) cations in the mineral surface become high spin (Fe(II) in bulk mackinawite is low spin), thereby increasing its potential for electron transfer.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Atmospheric CO₂ starvation of trees arrests mycorrhizal-driven silicate weathering

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Trees dominate terrestrial silicate mineral weathering by converting solar energy into chemical energy that fuels roots and their ubiquitous nutrient-mobilizing fungal symbionts. These biological activities regulate atmospheric CO₂ over geological timescales by driving calcium and magnesium fluvial ion export and marine carbonate formation. However, the important stabilizing feedbacks between CO₂ and biotic weathering anticipated by geochemical carbon cycle models remain untested. This presentation will show experimental evidence for a non-linear feedback across a Cenozoic CO₂ range from 1500ppm to 200ppm, whereby low CO₂ curtails mineral surface alteration via trenching and etch pitting by arbuscular mycorrhizal and ectomycorrhizal fungal partners of tree roots. Integrating our experimental findings into a process-based model revealed a CO₂ drop from 1500ppm to 200ppm caused the flux of calcium and magnesium weathered from silicate rocks to drop three-fold. It is proposed that 'low' CO₂ effectively acts as a ‘carbon starvation’ brake on tree-driven weathering. These findings have implications for the role of forests and fungi in regulating Earth’s minimum atmospheric CO₂ concentration over the Cenozoic.

Ore deposits and lithosphere evolution in the early Earth

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Plate tectonic processes, including subduction-related magmatism, rifting and collision are critical for the formation of many types of magmatic and hydrothermal ore deposits. Given the evidence for the existence of plate tectonic processes from as early as 3.9Ga, the absence of significant mineral deposits older than about 3Ga is attributed to either of a failure to survive, or the absence of another key ore-forming environment. Subcontinental Lithospheric Mantle (SCLM), which appeared between ca 3.6-3.0 Ga, provides the solution to understanding both of these issues. Pristine SCLM, formed as a residue of high temperature plume melting, is depleted (Fe-poor), buoyant, refractory, and has very high viscosity. These traits make for a durable lithosphere, a home for mineral deposits, in contrast to the easily removed (subducted, delaminated) dense oceanic lithospheric mantle. Integration of geological, geophysical and geochemical data from the crust and mantle, indicates that Archean SCLM underlies the majority of today's continental crust. Plate tectonics (forces, fluids, magmas) has resulted in metasomatism, fracturing, melting and suturing of the SCLM. These processes, along with the impact of mantle plumes and the rise of atmospheric oxygen, have provided the metals, energy and focus for ore systems in a range of associated crustal environments.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Seismic anisotropy changes across upper mantle phase transitions

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Constraining mantle flow near the mantle transition zone (MTZ) can help better understand its role in Earth’s thermochemical evolution and mantle dynamics. Using a higher mode surface wave seismic dataset [1] we modeled global 3-D azimuthal anisotropy in the top 1000km of the mantle, thereby providing constraints on mantle deformation to much greater depths than in previous studies.

Our model unravels significant seismic anisotropy in the MTZ, challenging common views of mantle deformation, and reveals a striking correlation between minima in anisotropy amplitudes, changes in the fast axes of propagation, and the location of phase transitions. This relation between anisotropy changes and phase transformations suggests lattice preferred orientation of anisotropic material in the deep upper mantle.

The detected global changes in the fast axes could indicate mantle flow layering, consistent with mantle geochemistry. The interpretation of our results in terms of convection style and therefore in terms of heat transport is however non-unique due to a lack of laboratory data on MTZ mantle anisotropy. Seismic anisotropy might not be a good proxy for mantle flow at these depths, in which case whole mantle convection cannot be ruled out.

Nevertheless, our model provides unique new constraints on mantle deformation and advances toward a better understanding of Earth’s convective pattern and heat transport will require stronger constraints on the effects of pressure, temperature, melting, and water content on the deformation mechanisms and slip systems of MTZ materials.

Constraints on the Composition of the Lower Continental Crust from Joint Inversion of P- and S-wave Seismic Velocity Data

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Seismic velocity data constitute one of the primary constraints on the bulk composition of the lower continental crust. P-wave velocity data are frequently used to infer the composition of the deep crust and to support petrologic models for the origin of the continental crust. Unfortunately, recent work has demonstrated that a large range of compositions can be associated with the same P-wave velocity, rendering the interpretation of these crustal velocity models to be highly non-unique. Alternatively, the ratio between P- and S-wave velocity (Vp/Vs) can be directly inferred from receiver function studies (though not the absolute P- or S-wave velocity). However, Vp/Vs ratios alone also lead to highly non-unique estimates for lower crustal composition.

In order to provide more robust constraints on lower crustal compositions, we calculate elastic properties for an expansive suite of crustal compositions (anhydrous and hydrous) and invert for major element chemistry as a function of P- and S-wave velocity over a range of pressure and temperature conditions. We show that the combination of P- and S-wave data significantly improves compositional resolution, particularly when a priori pressure and temperature constraints can be used to determine whether the lower crust resides in the alpha- or beta-quartz stability field.

We apply this inversion technique to a range of geologic settings with high quality P-wave S-wave data (e.g., cratonic North America, the African and Indian shields, and the Aleutian arc crust—which may represent a building block for continental crust). Compositional models for each region are derived based on expected crustal geotherms, along with complementary estimates for lower crustal properties including density and viscosity. These data are then used to test different models for crustal evolution.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org

Geodynamic implications from element fluxes in the Tonga-Lau system

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It is well known that lavas from active back-arc spreading centres contain a 'subduction component' (e.g. high Pb/Ce, U/Nb), the strength of which decreases with increasing distance of the spreading axis from the volcanic arc. However, it is not well understood how the Ba-, Pb- and U-rich subduction component is transported from the subducting plate to the shallow melting zone underneath the ridge axis. Many tectonic models for subduction zones assume vertical transport of fluid or aqueous melt from the surface of the subducting slab to shallower levels beneath the back-arc spreading axis, and the decreasing subduction signal with distance from the arc is thought to result from a decreasing fluid release from the subducting slab at greater depths. To test these hypotheses, we present new data from the Tonga-Kermadec arc, a 3000 km long arc in the southwestern Pacific, along with new and published data from the Valu Fa, Central and Eastern Lau back-arc basin spreading centres. The distance between the arc and back-arc increases from less than 10 km at ~23°S to ~150 km at 19°30’S, allowing the interaction between the arc and back-arc melting regimes to be constrained. Assuming that Nb is immobile in fluids, and that Ba/Nb, Th/Nb ratios are not fractionated during melting, we map out the subduction-related enrichment of Ba and Th underneath the Tonga Arc-Lau Basin system, and show using mass-balance arguments that the simplistic model of vertically rising fluids or melts is unrealistic. We suggest that the overlap in melting zones beneath the arc and beneath the back-arc spreading centre allows horizontal flow of melt from beneath the arc towards the back-arc (i.e. in the opposite direction to the flow of solid mantle induced by plate subduction) at shallow levels in the mantle, and this best explains a subduction zone signature underneath the back-arc. Our work demonstrates for the first time that melt can be focussed from the extreme edges of the melting zone underlying an active spreading ridge to the ridge axis, over distances of up to 200 km. Our model provides an alternative explanation for (238U/230Th) > 1 in back-arc lavas, and indicates horizontal melt flow velocities of 0.4-1 m/y.
Contrasting style of Iron formations deposited before and after the GOE

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Iron Formations are typically interpreted to indicate anoxic deep-water conditions before the rise of atmospheric oxygen and ocean ventilation. However, deposition of iron formations continued after the Great Oxidation Event (GOE) in shallow-marine conditions above the fairweather wavebase. Their deposition on several continents at ca. 1.89 Ga has been linked to a mantle plume breakout event and indicates development of the shallow-water redoxcline in the global ocean separating deep-water, anoxic and ferruginous conditions from shallow-water oxic and well-mixed environments. Iron oxidation at the dynamic redoxcline has been linked to iron-oxidizing microbial ecosystems, oxygenic photosynthesizers, and abiotic iron oxidation. In contrast, Archean iron formations were typically deposited below the storm wavebase and lack indicators of wave or storm activity. Conspicuous absence of Archean iron formations with granular structures and Fe-coated grains might indicate lack of mechanisms for quantitative iron oxidation in Archean shallow-marine settings, suggesting that oxidizing conditions and a strong redoxcline were lacking even in highly productive shallow-water settings. Iron isotope values of Archean and Paleoproterozoic iron formations are also consistent with non-quantitative Fe-oxidation in the Archean oceans arguing against a significant role of oxygenic photosynthesis in deposition of Archean iron formations. It seems therefore likely that anoxygenic photosynthesis in depositional settings with low sedimentation rates is responsible for deposition of Archean iron formations. The prediction from the contrasting style of deposition of iron formations before and after the GOE is that deposition of iron formations occurred at lower sedimentation rates before the rise of atmospheric oxygen. If this is the case, it has implications for scavenging capacity of iron oxyhydroxides and thus interpretation of geochemical records of iron formations.

Ge, related trace elements, and Ge isotopes in sphalerite from the Saint-Salvy deposit (France) by LA-ICP-MS and MC-ICP-MS.

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The recent increasing worldwide demand in germanium (Ge) encourages research for the understanding its geological cycles and the factors controlling its concentration in minerals. Ge occurs in a wide variety of geologic environments and though it averages 1.6 ppm in the Earth’s crust, high Ge contents may occur in both oxide and sulphide minerals (up to 100–3000 ppm), especially sphalerite so that Zn ores represent a major source of Ge, with coal. The Ge-bearing sphalerite of the Saint-Salvy Zn-Ge-Ag-(Pb-Cd) vein-type deposit was subjected to an integrated mineralogical, geochemical and Ge isotopic study in order to understand the mechanisms and processes that conduct Ge and related minor/trace elements (e.g. Cu, In, Ga, Ag, Sb, Sn) to be enriched in sphalerite regarding source, transport, and deposition conditions.

In situ analyses of trace elements using LA-ICP-MS, coupled with optical and electron microscopy and multivariate statistics, pointed out an opposite distribution of Ge between compositional zoning types in sphalerite, with contents ranging from 15 to 2580 ppm. In rhythmic bandings, Ge anticorrelates with Fe, Cd, In and Sn, and averages 500 and 200 ppm within light brown and dark brown bands, respectively. In sector zonings, Ge is enriched and correlates with Cu, Ga, Sb, Ag and As, and averages 1100 ppm. Cu would enhance the incorporation of trace elements, being involved in many coupled substitution mechanisms, among which the most notable: 2Zn 2+ ↔ Cu++ Sb3+. In addition, the main coupled substitutions 3Zn 2+ ↔ Ge4++2Ag+ and 3Zn 2+ ↔ In3++ Sn3+ also occur. Trace element features of the sphalerite from Saint-Salvy compared with those of other deposits worldwide revealed to be efficient to discriminate among genetic types of ores, which may find interests in exploration guidance. Bulk Ge isotope analyses by MC-ICP-MS showed δ47Ge, ranging from -1.97 to +1.01‰ (±0.25‰ ±0 SD) that positively correlate with Ge content and highlight large sub-surface fractionation processes during sulphide precipitation in low temperature hydrothermal open system.

Funded by LABEX RESSOURCES21 (ANR-10-LABX-21).

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
**Photophysical studies of biologically produced macromolecules**

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The attachment of microbes to solid surfaces is controlled by the macromolecular structure of the cell wall as much as driven by functional genes that are induced to produce cell wall macromolecules. We present here a quantification of the molecular conformation and sorption forces involved in the attachment of cell wall macromolecules such as lipopolysaccharides (LPS), alginites and extracellular polymeric compounds (EPS) extracted from bacteria. Our hypothesis is that the molecule-surface interfacial forces mediate the physicochemical interactions of bacteria cell wall, and its adaptation to the host environment. Photophysics studies (TRAMS), fluorescence and ICP-MS. The alumina and silica presence of alumina and silica using Time resolved anisotropy techniques were used to investigate adsorption of biopolymer onto mineral surfaces which should act as model systems for bacterial growth. Adsorption of dilute aqueous solution of macromolecules was studied as a function of pH in the presence of alumina and silica using Time resolved anisotropy studies (TRAMS), fluorescence and ICP-MS. The alumina and silica particles were used to mimic active sites existing on the surface of kaolin-like particles. It was found that LPS for example, had a high adsorption affinity for Al₂O₃ and in contrast adsorbs weakly to SiO₂ surface. Strong adsorption was observed at low pH for both minerals. The dependence of adsorption on the mineral concentration was also examined at different pH conditions: the adsorption amount was observed to increase by increasing the mineral concentration. Macromolecular folding and conformation of the LPS, alginate and EPS at the solid-solution interface was also quantified using TRAMS. The results showed a high pH and ionic strength dependence demonstrating that macromolecule adsorption is favoured and mediated by ions such as H⁺ and Ca²⁺ in solution. These findings indicate that proton bridges and van der Waal forces are responsible for interactions at the interface. A model for macromolecule adsorption at the interface including the role of ions in solution and folding was proposed. This model is representative of the behaviour of biological macromolecules at the aqueous-surface interface in natural environments. The processes described here have a direct implication on bacteria mediated mineralisation via concentration of ions from solution.

**Magmas, solutions and metals**

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Holland[1] demonstrated experimentally that Cl-bearing magmatic-hydrothermal aqueous fluids can scavenge metals from silicate melt and transport the metals into the surrounding crustal environment where fluid-rock reactions and decompression may cause metal precipitation and formation of deposits. Specifically, the abundance of Cl in the fluid phase was demonstrated to be a master variable that controls the total mobilized quantity of metal. Holland[1] stated: “It remains to be seen just how useful these criteria will turn out to be; the results of preliminary tests are encouraging”. This was a prescient statement indeed. Over the ensuing four decades, scientists have constructed a wonderful house of experimental knowledge on the scaffolding that Holland built, and these data guide our understanding of the incredible role of aqueous fluids in magmatic-hydrothermal systems.

Our research group continues to investigate experimentally the mobility of transition row metals, high field strength, and rare earth elements in aqueous fluids ranging from those exsolved from silicate melt in shallow-level magma chambers to fluids evolved during the blueschist to eclogite transition in subduction zones. Specifically, we are investigating how the complexity of aqueous fluid, i.e., dissolved chloride salts, fluorine, albite, etc., affects element mobility.

Data for the mobility of iron in a silicate melt – aqueous fluid – magnetite – sulfide assemblage indicate that the mass transfer of iron can moderate oxygen fugacity, sulfide stability, the composition of ferromagnesian silicates, and the fractionation of stable iron isotopes. These data have important implications for using iron as a geochemical fingerprint for processes that form porphyry, high-sulfidation, iron-oxide-copper-gold (IOCG), and iron-oxide-apatite (IOA) deposits. New data for the mobility of iron in a silicate melt – aqueous fluid can scavenge metals from silicate melt and transport the metals into the surrounding crustal environment where fluid-rock reactions and decompression may cause metal precipitation and form deposits.

Holland[1] demonstrated experimentally that Cl-bearing magmatic-hydrothermal aqueous fluids can scavenge metals from silicate melt and transport the metals into the surrounding crustal environment where fluid-rock reactions and decompression may cause metal precipitation and formation of deposits. Specifically, the abundance of Cl in the fluid phase was demonstrated to be a master variable that controls the total mobilized quantity of metal. Holland[1] stated: “It remains to be seen just how useful these criteria will turn out to be; the results of preliminary tests are encouraging”. This was a prescient statement indeed. Over the ensuing four decades, scientists have constructed a wonderful house of experimental knowledge on the scaffolding that Holland built, and these data guide our understanding of the incredible role of aqueous fluids in magmatic-hydrothermal systems.

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**DOI:10.1180/minmag.2013.077.5.2**

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Solubility of Nickel Ferrite (NiFe₂O₄) from 100 to 200°C

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Nickel ferrite is one of the oxides present on surfaces of the components of the primary circuit of pressurized water reactors (PWR). Its dissolution contributes to the release of nickel in the primary water, at the origin of the contamination phenomenon. A complete understanding of the behavior of nickel in the primary circuit must include solubility measurements of nickel oxides, including mixed oxides such as nickel ferrite.

The solubility of nickel ferrite was measured in a Hydrogen-Electrode Concentration Cell (HECC), which has been described in [1], at temperatures of 100°C, 150°C and 200°C and measured in situ pH between 4 and 5.25. The experimental solution was composed of HCl and NaCl (0.1 mol.L⁻¹). Based on previous studies ([2,3]), pure nickel ferrite was experimentally synthesized by calcination of a mixture of hematite Fe₂O₃ and bunsenite NiO in molten salts at 1000°C for 15 hours in air. The so obtained powder was fully characterized. After the experiment, the powder showed no significant XRD evidence of Ni(II) reduction. Nickel concentration was measured by atomic absorption spectroscopy and iron concentration was measured by UV spectroscopy. The protocol has been designed to enable the measurement of both dissolved Fe(II) and total iron [4].

The solution was slightly undersaturated relative to nickel oxide [1] and to both hematite and magnetite. The nickel/iron ratio indicated a non stoichiometric dissolution. The solubility measurements were compared with equilibrium calculations using the MULTEQ database. The solubility of nickel ferrite in a reducing acidic solution is reasonably well described by the available thermodynamic data.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org

Alternative nitrogenases in terrestrial ecosystems?

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Recent studies have shown that molybdenum (Mo), which is used in the Mo-nitrogenase, can limit N₂ fixation in temperate and tropical ecosystems. This suggests that alternative nitrogenases, which use V or Fe in place of Mo, may contribute to N₂ fixation. The acetylene reduction assay (ARA) is commonly used to estimate N₂ fixation but requires the use of an adequate conversion ratio (R ratio = acetylene reduction/N₂ fixation). The theoretical value for R is 3-4, but measured values in the field range from less than 1 to more than 10. In this study, we show that even in pure cultures, the R ratio is variable and dependent on the culture growth phase. Nonetheless, low R values (below 2) can be consistently attributed to N₂ fixation by alternative nitrogenases. Interestingly, an analysis of the literature shows that low R ratios are measured almost exclusively in soils, and are not found in the surface oceans (where Mo is abundant, and alternative nitrogenases are unlikely to be important) or in plant symbioses (which do not possess the genes for the alternative nitrogenases). The low R ratios may thus be indicative of alternative nitrogenases in soils. In a series of microcosm experiments with temperate soils from New Jersey, we were able to confirm that alternative nitrogenase genes were present, and expressed, even though N₂ fixation did not appear to be Mo-limited. The R ratios were low at the beginning of the incubations, suggesting that alternative nitrogenases contribute to the bulk to N₂ fixation in these samples. The R ratios also tended to increase over time, possibly reflecting depletion of the fixed carbon pool, or increased contribution from the Mo-nitrogenase. The possibility that alternative nitrogenases may contribute to N₂ fixation in systems that are not Mo limited is intriguing and deserves further investigation.

DOI:10.1180/minmag.2013.077.5.2
Development of the La-Ce systematics: application to arc magmas

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In the 1980’s, the 138La-138Ce systematics (T1/2 = 302 Ga) has been developed [1,2]. Since La/Ce fractionation is strong in some suprergene conditions (due to the occurrence of Ce4+), this isotope system is able to offer new information on the material involved in the genesis of magma in subduction zones. Here, we present Ce isotope data measured on Martinique lavas that have been thoroughly characterized in a previous study [3].

The Ce purification involves 3 steps: 1) REE isolation in HCl medium on cationic resin; 2) La-Ce-Pr-Nd separation using 2MLA acid; 3) purification of the Ce fraction using LnSpec resin. The Ce isotopic compositions were measured as the oxide species by TIMS, (Triton). In order to increase the signal size of the two minor isotopes (136Ce and 138Ce), 140Ce was not measured. The oxygen isotope composition is determined in situ following the method developed by [4]. The 138Ce/142Ce ratios are normalized to 136Ce/142Ce=0.01688. The 138Ce/136Ce ratio measured in the AMES standard is equal to 1.33745 ± 0.00001 (n=10, or 138Ce/142Ce=0.0225761 ± 0.000007), in agreement with previous measurements [2]. The 138Ce/142Ce ratios measured on the standard basalts BHVO-2 and BCR-2 are 0.0225662±0.000001 (n=13) and 0.0225684±0.000003 (n=3), respectively. The Ce purification involves 3 steps: 1) REE isolation in HCl medium on cationic resin; 2) La-Ce-Pr-Nd separation using 2MLA acid; 3) purification of the Ce fraction using LnSpec resin. The Ce isotopic compositions were measured as the oxide species by TIMS, (Triton). In order to increase the signal size of the two minor isotopes (136Ce and 138Ce), 140Ce was not measured. The oxygen isotope composition is determined in situ following the method developed by [4]. The 138Ce/142Ce ratios are normalized to 136Ce/142Ce=0.01688. The 138Ce/136Ce ratio measured in the AMES standard is equal to 1.33745 ± 0.00001 (n=10, or 138Ce/142Ce=0.0225761 ± 0.000007), in agreement with previous measurements [2]. The 138Ce/142Ce ratios measured on the standard basalts BHVO-2 and BCR-2 are 0.0225662±0.000001 (n=13) and 0.0225684±0.000003 (n=3), respectively. The 138Ce/142Ce ratios of the Martinique lavas define a large range (0.0225660 – 0.0225706) showing that the Ce isotopic system can be a powerful tool to trace heterogeneities in the source of arc lavas.

The Ce isotope tracer applied to 30 Martinique lavas shows a clear correlation with Nd, Sr and Pb isotopes suggesting a varying contribution from sedimentary material. Complementary data on sediments located in front of the arc should provide further constraints on the mixing relationships between sedimentary components and the mantle wedge underlying the Lesser Antilles arc.


Rb and Sr adsorption at the Quartz(101) – water interface

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Quartz is an abundant and ubiquitous rock-forming mineral in Earth’s continental crust, and influences the chemistry of numerous aqueous systems [1]. The sorptive property of quartz changes the mobility of ions in water while its dissolution process controls long-term silica cycling through the earth system. Batch experiments [2,3] showed that the dissolution rate of quartz at near-neutral pH increases substantially in the presence of cations while the degree of enhancement depends on the choice of cation. However, the detailed understanding on the mechanism remains unclear mainly because of the lack of atomic-scale information on the processes to explain the complexity of the interface chemistry. Molecular-scale investigation of the quartz surface-cation interaction is the first step in understanding this cation-induced mechanism. Here, we report on Rb+ and Sr2+ cation adsorption at the quartz(101)-water interface observed in 10mM salt solutions at pH 10 using x-ray reflectivity (XR) and resonant anomalous XR measurements.

The best fit models of the experimental data suggest that Rb+ adsorbs at an average height of 2.7 Å above the surface (defined as the average position of the two terminal oxygens), which may be a mixture of inner- and outer-sphere species. Adsorbed Sr2+ is prevalently located at 4.6 Å above the surface, suggesting the formation of an outer sphere complex. The occupancies of these complexes with respect to the unit cell area (UC) are 0.19 Rb+/UC, and 0.07 Sr2+/UC. The smaller coverage of Sr2+ compared to that of Rb+ is likely due to the difference in cation valency. The charge of the quartz(101) surface calculated based on the coverages at pH 10 is approximately 0.14 to 0.21 e-/UC or ~1 e- for 5 to 7 UC.

Pyroxenites from mantle section of Voykar Ophiolite (Polar Urals) – pathways for melt and fluid migration

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Late stages of formation of rocks from mantle section of Voykar Ophiolite were shown to take place in SSZ environment [1,2]. Dunite bodies and pyroxenite veins mark different stages of melt migration [2]. Best evidence for SSZ environment is preserved in mineral compositions from pyroxenite veins – high #Cr of spinel and LILE enrichments in Cpx and high-Al amphibole. Pyroxenite compositions display variability which is a function of their modal compositions, morphological features and spatial location.

Minerals from orthopyroxenites usually have high mineral #Mg, are most depleted in incompatible elements, show low Al in pyroxenes and spinel (#Crbel >0.6). Other group of pyroxenites with high mineral #Mg is represented by thin (cm-scale) clinopyroxenites and websterites and complex dunite-pyroxenite veins. Their major element compositions were equilibrated with adjacent harzburgites. Minerals from thicker websterites and clinopyroxenites have lower #Mg and subparallel boninitite-like trace element patterns of Cpx [1]. Cpx compositions across harzburgite-pyroxenite contacts show depletion in HREE (opposite to harzburgite-dunite contacts) and Zr enrichment in LREE and Sr. High-Al amphibole from websterites display trace element patterns with different LREE/HREE and MREE/HREE ratios, which could reflect their formation from melt to fluid-like agent.

Therefore, Voykar mantle section pyroxenite veins represent pathways for melts variously depleted in incompatible elements or in some cases fluids with boninite-like trace element patterns and elevated silica contents. Those melts were produced by melting of hybridized mantle source formed as a result of transformation of mantle olivine to orthopyroxene under the influence of slab-derived fluids/melts [2]. Different areas of massif could be arranged in order of increasing HREE contents in Cpx from dominated type of pyroxenite which could reflect relative depth or degree of melt fractionation.


New insights into the history of an ophiolite from zircons

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The Coolac Serpentinite Belt is part of the Tumut ophiolitic complex in the Lachlan Fold Belt, southeastern Australia. The 63 km belt contains a high proportion of massive (unfoliated) ultramafic rocks that have undergone only lower greenschist-facies metamorphism [1]. New U-Pb, Hf- and O-isotope and trace-element data have been obtained for zircons from the rocks of the belt. These include zircons separated from two (high-Al and high-Cr) massive chromitites and rodingites and grains recovered from gullies draining mainly weakly serpentinisated massive porphyroclastic harzburgite. The Belt is either faulted against, or intruded by, the S-type Young Granodiorite. Zircons from the Young Granodiorite collected at the contact with the serpentinite belt were also studied to refine the tectonic relation and timing of the granitic magmatism.

The U-Pb age obtained on the zircons from the serpentinite belt display a wide range of ages, from Silurian to Paleo-Proterozoic, with the main age population clustering around 430 Ma. This main peak coincides within the analytical error with the age obtained for the Young Granodiorite (427.6 ± 3.2 Ma) and inherited zircon ages for plagiogranites from the Belt [1]. The ages for the inherited zircon populations in the granodiorite correlate well with the older zircon populations from the Coolac ultramafic rocks.

Most of the Coolac zircons have negative εHf and heavy (>6) δ18O indicative of a crustal origin. Combined with U-Pb age information, this implies that the zircons in the peridotites are xenocrystic. One possibility is that zircons derived from subducted sediments were incorporated into the ophiolitic rocks (as in the Luobusa (Tibet) ophiolite [2]). However, the similarity of the Coolac ophiolite-derived zircons with those from the Young Granodiorite may indicate that they were introduced into the Coolac peridotitic complex during the granitoid magmatism and thus may carry no information on the origin of the Tumut ophiolitic rocks. In the latter case, the Coolac rocks should be older than the granitoid magmatism of the 420–390 Ma age of the Lachlan Fold Belt.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Monomeric and polymeric silica sorption on calcite

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Literature data about sorption of dissolved silica by calcite is fairly sparse and contradictory. Klein and Walter [1] investigated silica uptake at pH 6-8.3 and reported adsorption to be strongly pH dependent, with a maximum at pH 6. On the other hand, in flotation studies where sodium silicate was used as a depressant to suppress the flotation tendency of calcite, the experiments were mostly performed at pH > 8 and silica adsorption by calcite was reported to reach maximum at pH 9 to 10 [2, 3, 4]. In addition, the role of silica polymer adsorption in suppressing calcite flotation is unclear. Some authors [2] did not find any relationship with polymeric silica while others [3, 4] reported polymer adsorption to be responsible for suppression. Our study aimed to clarify the pH dependence of silica uptake by calcite and the importance of silica polymers in the process.

We investigated sorption of dissolved silica on calcite at 25 °C in calcite equilibrated solutions with pH ranging from 6 to 11, with varying initial silica concentration (≤ 2 mM) and surface area to liquid ratio (≤ 480 m²/L). The experimental conditions were designed such that polymeric silica introduced with the concentrated stock solution is stable at pH > 9 but unstable at lower pH.

Silica uptake was observed to increase with pH. At pH 11, almost 50% of the dissolved silica was removed from the solution, while no silica sorption was found at pH 6.1. The presence of stable silica polymers at pH > 9, is at least partly responsible for this pH dependence. At pH 8.3, we observed a significant, but temporary uptake of silica. It was released again to solution after several hours. This is consistent with silica being dominantly adsorbed as polymeric species and desorbed in response to depolymerisation.


Melt evolution from the mantle wedge to the crust: insights from South Kamchatka and West Bismarck arc xenoliths

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Rare xenoliths carried by recent andesites or arc theolites are the only direct witnesses of active sub-arc processes. We present a detailed study on such xenoliths from Avacha volcano in southern Kamchatka (Russia) and Ritter volcano, West Bismarck Arc (Papua New-Guinea Region). Avacha is located on a 'mature' subduction zone (~120 km Pacific slab depth, ~40 km crustal thickness). Harzburgites cut by websteritic veins, as well as massive olivine- and hornblende-clinopyroxenites and hornblendites occur in Avacha andesitic deposits (~7000 yrs. BP). Based on the compositions of minerals, melt inclusions and interstitial glass, we infer that the websteric veins formed from high-Ca boninites (HCB). Unlike a previous study [1], this inference is consistent with recent reports of complementary low-Ca boninites (LCB) in these rocks [2]. Similar datasets show that clinopyroxenites and hornblendites crystallized respectively at Moho and mid-crustal depth, producing residual liquids similar to Avacha andesites. Modelling suggests that these ‘cumulate’ rocks can form from an ascending HCB melt, modified by fractionation and melt-rock reactions in the lithospheric sub-arc mantle.

Ritter is part of an active and complex subduction zone (~120 km depth for the Solomon Sea Plate slab and ~20 km crustal thickness). Harzburgites, pyroxenites and dunites are found in picritic arc theolites (~125 yrs. BP) from Ritter. We show with the same toolbox, that pyroxenites and dunites are former primitive sub-arc melt channels. Evidence for LCB percolation in veins through these samples supports the current generation of boninitic mantle melts, like for Avacha.

In line with literature datasets on exhumed arc sections, we propose that boninites are common primary mantle wedge liquids in various types of subduction zones. Supported by our dataset on harzburgites, this puts direct constraints on mantle wedge melting beneath arcs. The possible HCB-andesite liquid line of evolution leads us to re-examine melt ascent and element flux models for subduction zones.

Non-traditional stable isotopes and surface complexation models for ion binding to humic substances (NICA-Donnan) and oxide mineral surfaces (CD-MUSIC)

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Non-traditional stable isotopes (i.e. Zn, Fe, Ni and Cu) are increasingly used for environmental studies [1]. Considering the wide range of possible sorbents (Mn or Al oxides, phyllosilicates, carbonates, biologic surfaces…), the importance of the reactions at the sorbent/water interface for these numerous studies emphasized the importance of modelling approaches that are needed to quantify the isotopic fractionation of these elements caused by their sorption at mineral/water, organic moieties/water interfaces.

The present work will show how the use of EXAFS spectroscopy and CD MUSIC and NICA Donnan modelling can help to better understand the changes in isotopic ratio. Zn isotopic fractionation upon sorption onto Hydrous Ferric Oxide (HFO) and goethite will be discussed to assess the influence of reactions at the Fe-(hydr)oxide/water interface on the isotopic distribution of Zn [1]. The Zinc isotopic fractionation during interaction onto natural organic matter will be discussed. The Donnan Membrane device was successfully adapted for isotopic measurements and used to separate Zn bound to the PHA from free Zn<sup>2+</sup> ions in solution and allowed the measurement of isotopic ratios of free Zn<sup>2+</sup>. The NICA-Donnan model, is used to simulate the corresponding isotopic fractionation and the composition of free Zn in the Seine river, France and allows a better understanding of Zn isotope fractionation mechanisms associated with organic matter binding [2].


In-situ IR spectroscopic study of forsterite carbonation in wet-scCO<sub>2</sub>

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Capturing and storing CO<sub>2</sub> in basaltic formations is one of the most promising options for reducing the effects of energy production from fossil fuel on the Earth. These geologic reservoirs have high reactive potential for CO<sub>2</sub>-mineral trapping due to an abundance of divalent-cation containing silicates, such as forsterite (Mg,Si<sub>2</sub>O<sub>4</sub>). Recent studies [1–4] have shown that carbonation of these silicates is more effective in wet scCO<sub>2</sub> conditions, encountered near a CO<sub>2</sub> injection well, than in dry and/or CO<sub>2</sub>-saturated aqueous fluids. More interestingly, formation of magnesite under supercritical fluid conditions has been reported in some of these previous studies at temperatures as low as 35°C [3], in spite of its known sluggish formation under aqueous scenarios.

In this study, we used high pressure IR spectroscopy to investigate the carbonation of nanometer-sized forsterite at 35 and 50°C by systematically titrating water that subsequently dissolves in scCO<sub>2</sub> at 90 bar. The results show that at low total dissolved water concentrations, only highly structured adsorbed water and bicarbonate are detected at the forsterite surface. However, as the water concentration increases up to a critical value, but below H<sub>2</sub>O-saturated scCO<sub>2</sub>, a more liquid-like water film is detected on the forsterite particles, the bicarbonate concentration decreases and magnesite precipitates, as shown in our in situt IR spectra, as well as from ex-situ XRD, TGA and SEM analyses.

The results of these studies provide important insights into metal silicate carbonation mechanisms in low water scCO<sub>2</sub> environments. They reinforce the concept of a water threshold for carbonation to occur, which has also been demonstrated for steel corrosion in the presence of wet scCO<sub>2</sub> [5]. These results will also constrain thermodynamic models and molecular dynamic simulations used to predict mineral trapping extent in basaltic host rocks.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Mantle Potential Temperature Trend for the Central Atlantic Magmatic Province

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Recently published high precision geochronology by Blackburn et al. [1] dates each of eight basaltic magmatic events intruded and extruded during the Central Atlantic Magmatic Province (CAMP) over a 0.6 Ma time span. Each of the four major CAMP magma compositions including High titanium quartz normative, High Iron quartz normative, Low titanium quartz normative, and Olivine normative are represented. Geochemical data from a variety of sources are available for each of the eight basaltic units and being applied to PRIMELT2 software developed by Herzberg and Asimow [2] that will enable the determination of mantle potential temperatures. These data will enable us to calculate temperature trends that will have a direct bearing on the petrogenesis of CAMP magmatism. Preliminary data yield mantle potential temperatures for the mean High titanium quartz normative and Olivine normative primary compositions determined by Salters et al. [3] of 1394°C and 1449°C respectively. These temperatures are lower than the > 1500°C melting range generally applied to the mantle plume model but are consistent with decompression melting of a subduction enriched subduction metasomatized sub-continental lithospheric mantle source (SCLM). The temperature trend that we establish will allow us to further evaluate the application of mantle plume and SCLM source models to CAMP.


Planets, Minerals and Life’s Origin

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Four paradoxes stand astride any effort to understand how life originated on Earth:
(a) The Tar Paradox. Organic molecules, given energy and left to themselves, devolve into complex mixtures, “asphalts” better suited for paving roads than supporting Darwinian evolution. Any scenario for origins requires a way to allow organic material to escape this devolution into a Darwinian existence, where replication with imperfections, where the imperfections are themselves heritable, allows natural selection to avoid a tarry fate.
(b) The Water Paradox: Water is commonly believed to be essential for life. So are biopolymers, like RNA, DNA, and proteins. However, the biopolymers that we know find water corrosive. Any scenario for origins must manage the apparent need of life for a substance (water) this is inherently toxic to life.
(c) The Single Biopolymer Paradox. Even if we can make biopolymers prebiotically, it is hard to imaging making two or three (DNA, RNA, proteins) at the same time. At the same time, genetics versus catalysis place different demands on the behavior of a single biopolymer intended to support life. Catalytic biopolymers should fold, for example, while genetic biopolymers should not fold. Catalytic biopolymers should contain many building blocks; genetic biopolymers should contain few.
(d) The Probability Paradox. Some biopolymers, like RNA, strike a reasonable compromise between the needs of genetics and the needs of catalysis. However, emerging data suggests that RNA is more likely to deliver catalytic power that destroys RNA than catalytic power that makes RNA.

This talk will review experimental data that makes suggestions about early planetary environments and mineralogy that might avoid, mitigate, and possibly resolve certain of these paradoxes. Key are the presence of minerals, including borates and molybdates, that interact with organic species that are intermediates between atmospheric carbon dioxide and dinitrogen and RNA. Productive interaction requires as well a subaerial environment having only intermittent interaction with water. Recent data suggests that such environments might even be found today on Mars.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
An integrated isotopic-geologic view of early continental crust formation from the oldest rock record

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A cornerstone of Earth sciences for many years was the assumed complementary of mantle and crustal chemical evolution, with extraction and recycling of continental crust through time thought to be the main processes controlling the composition of the upper mantle. This view has been brought into question following discoveries of extinct nuclide signatures in Archean rocks (e.g. 142Nd, 182W) requiring early differentiation and/or a non-chondritic Earth. Linked to this are questions of which isotopic and geochemical monitors of continental crust formation processes and continental mass are most reliable.

Here we present an integrated geochemical and geologic examination of Archean continent formation with an emphasis on the patterns of 176Hf and 143Nd isotopic variations. Focus is on the largest extent of early crust located within the 3000 km2 Eoarchean Itsaq Gneiss Complex of SW Greenland. This complex preserves evidence of several temporally and spatially distinct episodes of juvenile crust formation between ~3.89 Ga and 3.66 Ga, which are dominated by TTG rocks. In each event, TTG suites were emplaced into slightly older gabbros, basalts and andesites, which have geochemical signatures consistent with fluid-fluxing of upper mantle sources. The TTG suites are characterized by magmatic zircon with initial εHf of ~0 and positive whole rock initial εNd of +4 to +2. The most likely geodynamic settings for generation of this early crust were convergent plate boundary environments analogous with, but not identical to, modern island arcs. The pattern of near constant εHf values in primitive granitoids for >300 m.y. argues against derivation of these magmas by repeated sampling of a mafic crustal source, from reworking of older crustal material, or from a mantle source previously experiencing large amounts of Hadean crustal extraction. Starting at 3.66 Ga, granitic rocks first begin to show Hf isotopic evidence for reworking of older crust. Varying 143Nd isotopic compositions of Eoarchean rocks likely reflect early Sm/Nd fractionation unrelated to crustal extraction. We propose that the shift to correlated 176Hf-143Nd isotopic temporal trends, as typify Phanerozoic style arc accretion processes, began as early as ~3.5 Ga.

Geochemistry and Carbon Management

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Without a doubt, meeting human energy needs while dramatically reducing greenhouse gases emissions is one of the grand challenges of our time. Geochemistry plays a critical role in assessing both the impacts of changing the chemical composition of the atmosphere due to emission of greenhouse gases and designing solutions. Over the coming decades, a radical transformation of our energy system is needed to reduce global greenhouse gas emissions by over 80%. Solutions for achieving needed emission reductions include improving energy efficiency, shifting to renewable energy resources for producing electricity, reducing emissions from fossil fuel by capturing and storing CO2, switching from coal to natural gas for power generation, and sustaining use of nuclear power. In this paper, the critical role that geochemistry plays in developing and evaluating solutions is highlighted. Examples from carbon dioxide capture and storage, nuclear waste disposal, shale gas development, and providing the critical materials for renewable energy and storage systems are provided. Over the coming decades, Earth’s resources will be taxed in new and unforeseen ways. The discipline of geochemistry will play a crucial role in anticipating and responding to these challenges.
Intracellular calcification by cyanobacteria: a significant controlled biomineralization process

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Cyanobacteria had a pivotal role on several global geochemical cycles throughout Earth’s history in particular, by biomineralizing CaCO3. Calcification by cyanobacteria has so far been considered exclusively as an induced extracellular biomineralization process. However, we recently discovered deep-branching cyanobacteria that form intracellular amorphous Ca-Mg-Sr-Ba carbonates [1]. The existence of such intracellularly calcifying cyanobacteria may modify significantly our view on the past and modern role of cyanobacteria in the formation of carbonate deposits and the degree of control they achieve on this geochemically important process. However, several questions remain open: is this biomineralization process widespread phylogenetically or restricted to one single species? Does it occur under specific or diverse environmental conditions? To what extent do phases formed intracellularly by these cyanobacteria differ from abiotically-formed carbonates?

We will address these questions using diverse approaches including high spatial and spectral resolution spectromicroscopies and molecular biology.

Figure 1: SEM image of Candidatus Gloeomargarita lithophora.


Polysulfides as intermediates in the bacterial metabolism of stored sulfur

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Zero-valent sulfur is a key intermediate in the microbial oxidation of sulfide to sulfate. Many sulfide-oxidizing bacteria therefore produce and store large amounts of sulfur intracellularly. It is still not well understood how the stored sulfur is metabolized as the most stable form of S0 under standard biological conditions – orthorhombic α-sulfur – can most likely not be utilized by bacterial enzymes.

In this study, the speciation of sulfur in single cells of living bacteria was investigated by Raman spectroscopy. Four different strains of Beggiatoa were used to compare the chemical nature of sulfur under various ecological and physiological conditions. Results showed that in microaerobic cultures at circumneutral pH, stored intracellular sulfur consisted of S8 rings and inorganic polysulfides (Sn2-). Linear sulfur chains were detected during both the oxidation and reduction of stored sulfur suggesting that Sn2- species comprise a pool of activated sulfur utilized by bacteria. The formation of Sn2- results from the cleavage of sulfur rings, either biologically by membrane-bound thiol groups and glutathione or chemically by the strong nucleophile HS-. It is likely that Beggiatoa in the environment utilize both of these mechanisms to generate Sn2- intermediates as they migrate vertically between oxic and sulfidic sediment zones.

With Raman spectroscopy it was possible to further track the fate of sulfur during its oxidation to sulfate. Unexpectedly high concentrations (up to ~2 M) of internal sulfate were detected in Beggiatoa sp. Although the reason for the intracellular accumulation of sulfate remains unknown we could show for the first time that Beggiatoa contain sulfate in concentrations 100-1,000-fold higher than that of the external environment.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Non-classical nucleation of minerals and the multiple roles of additives

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Recent reports have demonstrated the existence of stable clusters of calcium carbonate (CaCO₃) prior to nucleation through various experimental methods and also computer simulations [1, 2, 3, 4]. In contrast to classical notions, it appears cluster aggregation, not the assembly of their constituent ions, plays the significant role in nucleation of amorphous calcium carbonate (ACC), which later transforms into crystalline polymorphs.

This multi-stage process can be influenced by additives in several ways, which is of particular interest for biomineralization, as various additives, e.g. proteins, polysaccharides, and inorganic salts, are present throughout the nucleation processes. Though many systems have been investigated [5, 6, 7], the exact roles of additives are yet unknown, especially when it comes to mechanistic insights.

In the current contribution, we summarize the concept of non-classical nucleation of CaCO₃ by means of pre-nucleation clusters and recent advancements, including other mineral systems. Moreover, through potentiometric titration assays in the presence of additives, we exemplify the role of additives from simple salts to complex proteins on the early stages of precipitation, e.g. pre-nucleation cluster stability, time of nucleation, solubilities of the subsequently-formed phases, and on further phase transformations to the various crystalline polymorphs. Beyond insight into the fundamentals of biomineralization, understanding of the effect of additives on crystallization is also crucial in the creation of biomimetic materials and the formulation of novel anti-salant methods of industrial importance.


3D visualisation of core formation in deforming planetesimals

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Deformation may significantly enhance permeability of small fractions of metallic melt in a solid silicate [1]. This is an important factor in constraining processes of core formation, as a permeable network in solid silicate could have led to segregation of a core and mantle much earlier than previously thought, importantly long before the onset of a molten silicate ‘Magma Ocean’. Few experiments examine effects of low strain-rate deformation at realistic conditions of core formation in small planetary bodies. In addition, 3D melt geometry and permeability is usually inferred indirectly from 2D textural analysis of polished sample slices.

We have conducted experiments on a synthetic solid olivine – liquid FeS system at extreme P-T conditions using the rotational Paris-Edinburgh Cell (roPEC), and have analysed 3D melt geometry of quenched samples have using micro- and nano-tomographic imaging techniques. Deformation at strain rates as low as 10⁶ s⁻¹ aids grain boundary wetting and the formation of melt veins that appear to locally ‘drain’ certain areas of the sample. Results support theories of complex, multi-stage core formation in which pre-differentiated planetary bodies collided to form the Earth. These proto-cores may have sunk directly to the Earth’s centre without re-equilibration with the Earth’s mantle, which has major implications for the inferred geochemical composition of the lower mantle [2].

Voluminous outburst of silicic low δ18O magma in NE-Iceland inferred from zircon δ18O and U-Pb geochronology

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The Borgarfjörður Eystrí area in NE-Iceland represents the second-most voluminous outcrop of silicic eruptive rocks in Iceland and is a superb locality to unravel bimodal volcanism (c.f. “Bunsen-Daly” compositional gap), which has struck petrologists as abnormal for this tectonic setting for decades. Several explanations have been proposed; closed system fractional crystallisation, partial melting of hydrothermally altered crust, or partial melting of an underlying fragment of old continental or oceanic crust. To contribute to a solution to this issue we focus on zircon to unravel the origin, timing and evolution of voluminous evolved rhyolites in the Neogene silicic volcano complexes in the greater Borgarfjörður Eystrí area. We report zircon U-Pb geochronology and δ18O values measured by SIMS, and on whole rock δ18O values of felsic and intermediate units from Dyrfjöll and Breiðavik central volcanoes. With this new dataset we are able to decipher timing, primary magmatic processes, as well as contamination and/or post emplacement alteration. Zircon U-Pb ages of key units reveal prolonged silicic activity represented by several rhyolite flows at 12.26 ± 0.33 Ma and younger basaltic volcanism.

Pyroxenites and the construction of oceanic arc roots

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Pyroxenites are a major component of arc roots. They bear important information on the igneous and metamorphic evolution of arcs. In the Jijal and Sapat complexes of the Cretaceous Kohistan oceanic arc (Himalaya, Pakistan), pyroxenites formed by reactive flow of basalts within residual mantle peridotites [1,2]. In the Talkeetna Jurassic arc (Alaska), pyroxenites are high-pressure fractionation products of primitive hydrous basalts [3].

The Neoproterozoic Amalaoulaou oceanic arc root (Gourma belt, West Africa) exposes dykes of spinel and garnet pyroxenites cutting across layered garnet granulites and plagioclase pyroxenites [4]. Spinel pyroxenites were crystallized at about 1.0 Ga. Isobaric cooling down to 850-900 ºC induced the formation of garnet around spinel. In the vicinity of the pyroxenite dykes, lower crustal gabbros were partially molten leading to the formation of garnet granulites and garnet-clinopyroxene-rutile residues. Spinel pyroxenites were fractionated from a primitive hydrous basalt (Mg# ~ 60-70). Calculated equilibrium liquids are similar to melt-like hornblende gabbros forming the middle to lower crust of the Amalaoulaou arc. One peculiar orthopyroxene-rich spinel pyroxenite found as a xenolith within the garnet granulites shows high Mg# and Cr content but high incompatible elements contents (LREE, Zr, Nb). It is interpreted as a product of melt-peridotite reaction before the intrusion of the garnet granulate precursor.

The strong planar-linear, high-temperature fabric of spinel pyroxenites in dykes is oblique to layering and metamorphic foliation of garnet granulites. These dykes are representing magma paths where the primitive mantle-derived basalt differentiated en-route by segregation of pyroxene and spinel. The Kohistan and Amalaoulaou complexes do not display a thick sequence of cumulate pyroxenites [4]. Instead, scattered cumulate pyroxenites resulted from fractionation and/or melt-rock reaction in dykes or channels.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Fluoride in groundwaters of regolith and bedrock (0-900 meters depth) in a granitoid setting, SE Sweden

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Parts of Scandinavia show elevated fluoride in groundwaters which can be linked to the igneous host bedrocks of the Baltic Shield [1]. We investigated fluoride in groundwaters down to 900 meters depth in a small area located in southeastern Sweden. Just north and south of the study area intrusions of fluorine-rich (average 0.43 wt%) 1.45 Ga old granites are situated [2, 3]. Fluoride in private excavated wells are approximately five times higher here compared to Sweden in general [4]. Groundwaters in regolith (boreholes with plastic-casings; 0.3 mm slot screens) and fractures in the bedrock (boreholes with packed-off sections) were monitored for several years and were evaluated with respect to fluoride hydrogeochemistry. In addition, fluoride content in the host rock minerals have been investigated using wavelength dispersive spectrometry.

Fluoride in the regolith groundwaters ranged from below level of detection (LOD, <0.2 mg/L) to 5.1 mg/L (median 1.4 mg/L) and were overall stable over time. In the bedrock groundwaters, concentrations ranged from below LOD to 7.4 mg/L (median 2.7 mg/L). The area closest to the Götemar granite showed the highest fluoride concentrations in both water types, which suggests presence of F- rich secondary mineral coatings on fracture walls (fluorite is overrepresented here) and F-rich glacial deposits originating from the intrusion of the Götemar granite as major sources.

This granite and associated greisen contain higher amounts of F-rich fluorite and apatite, than surrounding rocks and in addition, biotite, muscovite and apatite are much more F-rich. Further on, the fluoride concentrations in the bedrock groundwaters increased closer to the surface in waters classified as of meteoric origin [5]. This pattern may indicate a downward transport of fluoride from the regolith into the bedrock fracture system.


Carbonate clumped isotope thermometry in the subsurface

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The carbonate clumped isotope thermometer potentially can be used to reconstruct the temperature and d18O of the ocean in the distant past. However, there is considerable uncertainty regarding how the thermodynamically controlled, temperature dependent abundance of carbonate groups containing both 13C and 18O, is affected during burial. There is evidence that both recrystallization and solid state diffusion within the crystal lattice are important processes. There is likely a time-depth dependence to these processes, though the details of these dependencies are currently poorly constrained.

This study explores how the burial and exhumation history modifies the primary distribution of isotopes in host carbonates from the subsurface and surface of Oman. The study includes rocks of Eocene to Neoproterozoic age that sit at current burial depths of 360 m to 5850 m. Additionally, we analyzed exhumed carbonates from the same formations, estimated to have been buried from 1-2 km up to 8-10 km.

Results from this work suggest two dominant modes of diagenesis: 1) Texturally well preserved carbonates measured from the subsurface yield seawater compositions similar to today of around 0% with Phanerozoic samples yielding temperatures <40°C and Neoproterozoic samples yielding temperatures <60°C. 2) Highly recrystallized carbonates affected by low-water-to-rock diagenesis sit close to the current geothermal gradient. Samples exhumed from depths >8km yield higher temperatures (120-150°C) and very enriched fluid compositions (~8‰) and also indicate low water-to-rock diagenesis.

DOI:10.1180/minmag.2013.077.5.2

www.minersoc.org
From shale oil to shale gas: mineralogical and geochemical evolution of Barnett Shales

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Tight oil is a rapidly growing unconventional energy resource that is increasingly viewed as an abundant global commodity. An issue is that tight oil reservoirs are highly heterogeneous. As a result, fluid production assignments and mixing, drainage zone definition and reservoir performance remain poorly constrained. Here, we report the characterization of samples from the organic-rich Mississippian Barnett shale gas system (Fort Worth Basin, Texas, USA) at varying stages of thermal maturation. Using a combination of compositional organic geochemistry and spectromicroscopy techniques, including transmission electron microscopy (TEM) and scanning transmission X-ray microscopy (STXM - 5.3.2.2. ALS STXM Polymer beamline [1] - 10ID-1 CLS SM beamline [2]), we document the mineralogical and geochemical evolution of the investigated samples and evidence the net increase in sample geochemical heterogeneity with increasing maturity [3]. We distinguish kerogen from bitumen in samples of oil window maturity from the estimation of aromaticity and polarity using STXM-based XANES spectroscopy. The formation of nanoporous pyrobitumen has been inferred for samples of gas window maturity, likely resulting from the formation of gaseous hydrocarbons by secondary cracking of precursor bitumens. By providing in situ insights into the origin and fate of organic fluids as a response to the thermal evolution of the macromolecular structure of kerogen, the present contribution constitutes an important step towards better constraining reservoirs within unconventional systems.


Flux particle size and composition effects on the evolution of sanitary-ware vitreous body

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A combination of three industrial flux compositions (sodium feldspar > 67 wt.%, potassium feldspar > 69 wt.% and a 1:1 mix of them) and two particle size distributions (d50 $\leq$ 45 and 75 μm) have been used to prepare sanitary-ware slips (flux amount about 25 wt.%). Samples have been fired up to 1200 °C, and then characterized in terms of water absorption, density, X-ray diffraction (at ambient and HT conditions) and micro-structure occurrence by Scanning Electron Microscopy. Despite of the small differences in the samples, some trends have been observed. Water absorption and interconnected porosity (obtained by density measurements) are minimized if sodium feldspar is used, suggesting a better densification, in agreement with [1]. The same effect is achieved by decreasing the flux particle size, which leads to a higher reactivity of the starting slip, in keeping with [2]. The application of RIR-Rietveld method [3] to powder diffraction patterns shows that also differences in phase composition are present: in particular, the highest glass content has been observed if the smallest flux particle size is used, in combination with a sodium bearing feldspar. Moreover, observations from HT-powder diffraction experiments (thermal range 900-1100°C) do not yield significant differences in the feldspar thermal decomposition as a function of flux composition and particle size.


DOI:10.1180/minmag.2013.077.5.2
www.minerssoc.org
Microbial extracellular polymeric substances modulate the product of uranium biomineralization

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Microbial biomineralization influences the cycling and sequestration of a variety of metals and metalloids in the environment. Uranium biomineralization by *Shewanella oneidensis* MR-1 was shown to produce two distinct U(IV) products under different chemical conditions. Here, we report that the uranium product is modulated by the formation of extracellular polymeric substances (EPS), a biological response that improves cellular resistance to U toxicity. When imaged by cryo-electron microscopy and analyzed by X-ray absorption spectroscopy, the two uranium products have distinct morphologies and atomic environments. This difference is shown to be due to the presence or absence of EPS using a spectroscopy method — scanning transmission X-ray microscopy (STXM)— that can differentiate amongst carbon biomolecules and localize U. When EPS is present, U is largely associated with it instead of the cell surface. Furthermore, we show that when the suspected U reductases are removed by mutation, EPS production and cellular viability decrease. Hence, the structure of the product of uranium biomineralization is intricately linked to the formation of EPS. We posit that a single U(IV) product is favored in the subsurface due to the prevalence of biofilms and because EPS are major component of those structures.

Hydromagnesite reactivity in aqueous solutions

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Hydromagnesite (Mg5(CO3)4(OH)2*4H2O) is the most common hydrous Mg-carbonate occurring at Earth’s surface environments. It usually forms as a secondary phase in alkaline and Mg-rich natural waters where magnesite (MgCO3) formation is inhibited by the strong hydration of aqueous Mg [1]. Formation of hydromagnesite is commonly mediated by microbiological activity [2], so that its dissolution and growth may be closely coupled to promoting primary productivity in aquatic environments.

A critical factor defining the role of minerals in natural processes is the link between their dissolution and precipitation rates. In accord with transition state theory, precipitation rates should be readily calculated from corresponding dissolution rates using simple functions of chemical affinity. This possibility has proven to be challenging to validate due to the difficulty in measuring the precipitation rates of most minerals in the laboratory. The relative ease to which hydromagnesite precipitates at ambient conditions makes it ideally suited to assess the link between dissolution and precipitation rates.

Hydromagnesite dissolution and precipitation rates have been measured in closed-system reactors from far to near to equilibrium conditions in NaHCO3/Na2CO3 bearing aqueous solutions at pH from 8.5 to 11.2 and temperatures from 25 to 75 °C. Resulting rates (r) have been modeled using:

\[ r = k(1-\Omega)^n \]

where \( k \) is the surface area normalized rate constant, \( \Omega \) the saturation degree of hydromagnesite, \( \sigma \) the Temkin's coefficient [3] (\( \sigma = 0.2 \)), and \( n \) the reaction order (\( n = 1 \)). Preliminary data interpretation suggests that the rate constants describing dissolution are from one to two orders of magnitude faster than those describing precipitation. For example, at 25 °C and pH 8.5 dissolution and precipitation rate constants were determined to be \( 3.0 \times 10^{-9} \) and \( 5.4 \times 10^{-11} \) mol/m2/s, respectively. Such differences could be attributable to the changing density of reactive sites on the mineral surface as a function of fluid saturation state.

Recovering and refurbishing of the SILNUC code, a tool to mitigate and prevent amorphous silica scaling

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Modelling the fate of silica in geothermal brines is of utmost importance to prevent and mitigate amorphous silica scaling both in surface installations and in the geothermal reservoir upon reinjection of spent fluids.

In principle, these theoretical predictions can be done using the software code SILNUC which was written by Weres and coworkers over thirty years ago. In practice, as far as we know, only the listing of this software is presently available in their report [1]. Thus, we decided to try to recover and refurbish this code.

SILNUC models the homogeneous nucleation and growth of colloidal particles of amorphous silica. It comprises three major algorithms.

The first one is the molecular deposition or particle growth algorithm. The Runge-Kutta approach is used to compute the particle radii and the dissolved silica concentration, both as a function of time. The second one is the nucleation algorithm, which simulates the generation of classes of colloidal particles. The third one specifies the temperature, pH, and fraction of water lost through steam separation as functions of time. Review of the recent literature is also planned during refurbishing of the SILNUC code.


The oxidation states of cerium and europium in silicate melts as a function of oxygen fugacity, composition and temperature


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Ce and Eu are the only rare earth elements (REE) to occur in oxidation states other than REE3+ under terrestrial magmatic conditions. The stability of Ce4+ and Eu2+ results in anomalous, chondrite normalised, abundances of these elements relative to the other REE due to the effect of oxidation state on trace element partitioning [1]. The link between oxidation state and oxygen fugacity (fO2) means that fO2 may be determined if Ce4+/Ce3+ or Eu2+/Eu3+ can be evaluated directly or inferred from the magnitude of an anomaly.

Ce and Eu LIII-edge XANES spectra were used to determine Ce4+/Ce3+ and Eu2+/Eu3+ in melts in situ [2], and quenched to glasses, as a function of fO2 (from -14 to +6 log units relative to the quartz-fayalite-magnetite, QFM, buffer), composition (MORB plus ten Fe-free systems), temperature (1200-1500 °C) and pressure (1 atm and 1 GPa). Ce4+/Ce3+ and Eu2+/Eu3+ vary systematically with the thermodynamically predicted dependence on fO2. For both elements higher oxidation states are favoured by less polymerised compositions (large values of optical basicity and NBO/T) and lower temperatures. Pressure appears to have a negligible effect. A general expression for Eu2+/Eu3+ in geological melts has been derived. An fO2 window, beginning near QFM, exists where both Ce4+ and Eu2+ are stable. Coexisting Ce and Eu anomalies in minerals such as zircon are thus not necessarily related to plagioclase fractionation. In Fe-bearing compositions, neither Ce4+/Ce3+ nor Eu2+/Eu3+ are preserved on quenching from a melt to a glass due to electron exchange reactions between Ce4+ and Fe3+ and Eu2+ and Fe3+. This limits oxybarometry to estimates of Ce4+/Ce3+ and Eu2+/Eu3+ determined from partitioning derived anomalies.

Experimental investigation of K incorporation into tourmaline at high temperature and pressure

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Tourmaline’s extensive stability in pressure-temperature space and ability to incorporate a multitude of elements in its structure have motivated investigation into its potential as a recorder of its formation conditions, especially in terms of temperature and composition [1]. However, the discovery of microdiamond-bearing K-dominant dravitic tourmaline, with up to 0.576 apfu K (2.76 wt.% K2O), in the Kokchetav Massif, Kazakhstan, [2] has increased interest in the relationship between formation pressure and tourmaline’s composition, particularly with respect to the incorporation of K. Indeed, a comparison of tourmaline’s composition with its inclusion mineralogy has revealed a correlation between K incorporation and increasing pressure [3]. However, whether or not the presence of microdiamond inclusions is sufficient evidence for high pressure formation of K-dominant tourmaline has been questioned [4].

A series of piston-cylinder and hydrothermal synthesis experiments was conducted to begin addressing the absence of experimental data on K-bearing tourmaline and to investigate the effect of pressure and fluid composition on the Na/K ratio of hydrothermal dravitic tourmaline (NaMg3Al6Si6O18(BO3)3(OH)3OH). Approximate unit cell dimensions were determined by Rietveld refinement of X-ray diffraction patterns and chemical formulae were calculated from electron microprobe analyses. To date, the highest pressure and temperature conditions investigated (40 kbar, 700°C) have yielded dravitic tourmaline with up to 0.7 apfu K when exposed to a pure KCl fluid. This is the first time Na-absent “potassium dravite” has been synthesized experimentally.


Deconstructing the dissimilatory sulfate reduction pathway: Isotope fractionation of a mutant unable to grow on sulfate

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Dissimilatory sulfate reduction plays a significant role in shaping the sulfur isotope composition of sedimentary sulfides, which are, in turn, a record of Earth’s surface redox history. The fractionation produced by this microbial metabolism is controlled by the flux of sulfur through the respiratory reaction network and the isotopic effect associated with each reaction. Although the net isotope fractionations of this metabolism have been well studied, unravelling the isotopic influence of each component of its pathway is still a challenge. The sulfite to sulfide reduction step is a particularly complicated one. Its full biochemistry is not fully understood and the associated isotopic effect is inferred from fractionations associated with the entire metabolic pathway. Here, we investigated a mutant strain of Desulfovibrio vulgaris Hildenborough in batch and continous culture to address these issues. This deletion mutant is missing its QmoABC complex, a principal enzyme in the reduction of adenine phosphosulfate (APS) to sulfite. Thus, this strain is incapable of using sulfate as a terminal electron acceptor. By hindering APS reduction, this mutation also eliminates sulfite disproportionation. In all experiments, lactate and sulfite consumption are concomitant with sulfide and thiosulfate production. Rates of thiosulfate production were one order of magnitude larger in batch than continuous culture experiments. Results from batch culture show a δ34S between sulfite and sulfide of ~9 ‰. The two components of the thiosulfate pool (sulfonate and sulfane moieties) present a large 34S/32S fractionation, with sulfonate more 34S enriched than sulfane by 30 ‰. However, the net fractionation between thiosulfate and sulfite is ~+1 ‰. This is inconsistent with isotopic observations of abiotic thiosulfate formation. Steady-state models are presented to understand the mechanism of fractionation during sulfite reduction and incorporate this step into the overall metabolism of sulfate reduction.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
**In-Situ Monitoring Of Water-Rock Interaction By Micro FT-IR- An Example Of Calcium Silicate Hydrate Formation-**

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In the geological disposal of high level radioactive wastes, cementitious grout materials are planned to be used and Calcium Silicate Hydrates (C-S-Hs) are supposed to be formed by water-rock interactions. The current study presents a new methodology of monitoring the C-S-H formation in situ by micro Fourier transform infrared (FT-IR) spectroscopy.

An in situ hydrothermal cell was constructed from titanium alloy with a diamond window to allow the transmission of an IR beam (Fig. 1). In this study, thin sections of quartz were placed in the cell, with the remaining space filled with saturated Ca(OH)₂ solution. The in situ hydrothermal cell was then sealed and heated at 140 °C at a pressure of 3 MPa. IR spectra were collected every 5 minutes for 24 hours using an IR microspectrometer.

![Fig. 1](image1.png)

**Fig. 1** The schematic figure of the in situ hydrothermal cell

**Fig. 2** Infrared spectral changes with time for 5 hours at 140 °C. The absorption band around 970 cm⁻¹ (C-S-H) increased with time.

An IR absorption band around 970 cm⁻¹ due to stretching vibration of Si-OH increased with time indicating the increasing formation of C-S-H (Fig.2). The temporal changes with 5 minute intervals of the peak heights in the first 240 minutes can be used to determine apparent formation rate constants of the C-S-H. Based on these experimentally determined kinetic parameters, mechanisms and rates of the C-S-H formation processes can be discussed.

**Water in Na montmorillonite - A neutron scattering study**

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Swelling clays, like Na montmorillonite, are important sealing materials for radioactive waste repositories. The negative charge of crystalline layers is compensated by cations surrounded by water in interlayers. At low hydration, all water is located in interlayers in up to 2 molecular water layers; at higher hydration, interparticle pores between clay particles also contain water.

To model and understand transport properties, e.g. water diffusion, it is important to know the water distribution at different hydrations and densities. Relative fractions of water in the two pore environments were measured directly and for the first time using Fixed Window scans on a neutron backscattering spectrometer. The decisive parameter was found to be the water content (total water / dry clay). In the range from 0 to 0.7 g/g the obtained water amount in the interparticle pores increases monotonically, but not linearly from 0 to 64%. These results were compared with values obtained based on surface area measurements.

They were also used to derive local diffusion coefficients from quasielastic neutron scattering. In the literature local diffusion coefficients can be found only for low hydrations (1 or 2 water layer) because of the difficulties in interpretation of the spectra when more than one water population exists. Here, from our combination of methods (quasielastic neutron scattering and fixed window scans) we can present local diffusion coefficients for up to 4 water layer in the interlayers.

DOI:10.1180/minmag.2013.077.5.2

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Carbon flow from volcanic CO$_2$ into soil microbial communities of a wetland mofette

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We investigated mofettes, i.e., cold volcanic CO$_2$ exhausts, in a wetland area in the NW Czech Republic. Here, continuous emanations of CO$_2$ lead to lower pH and anoxic conditions. Recent findings suggest that such alteration might cause a shift of the microbial community towards anaerobic and acidophilic organisms.

In this study we i) analyzed differences in the active archaeal and bacterial community structure in different depths of a mofette compared to the surrounding wetland soil by 16S rRNA pyrosequencing and ii) used DNA- and lipid-based 13C-CO$_2$ Stable Isotope Probing (SIP) to identify microbial communities which can incorporate the emanating CO$_2$.

16S rRNA pyrosequencing revealed that the overall active bacterial community composition was similar for the mofette and reference soil in all sampled depths. However, in the mofette soil Acidobacteria showed a higher relative contribution (55% to 70%) compared to the wetland reference (17% to 22%) primarily consisting of sequences closely related to Candidatus Koribacter sp. and isolate „Ellin 624“ of Subdivision 1. The active archaeal community of the mofette soil was dominated by methanogens in all depths which were not represented in the wetland reference soil.

Analysis of incorporation of 13C-labeled CO$_2$ into PLFAs and ether-lipid derived hydrocarbons in the mofette soil showed continuous enrichment over 28 days in almost all bacterial and archaeal biomarkers. Archaeal CO$_2$ utilization was restricted to the first 10 cm of the soil, while a depth-independent labeling pattern was found for bacterial biomarkers. Archaeal 16S rRNA and formyl tetrahydrofolate synthetase (fhs) gene labeling analysis of the first 10 cm suggested that CO$_2$ was potentially utilized chemolithoautotrophically by two novel groups of acetogens and methanogens, with the latter primarily being affiliated with the family Methanoregulaceae. On the other hand, bacterial 16S rRNA gene labeling analysis indicated a non-obligate autotrophic utilization of CO$_2$ by bacterial families of the Anaerolineaceae, unclassified Bacteroidetes and Syntrophaceae.

Characterization of hydrocarbon and functionalized silica nanoparticle adsorption on mineral surfaces through advanced First Principles techniques

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Atomistic simulations have come to play an increasingly important role in advancing understanding of the fundamental properties related to the hydrocarbon and nanoparticles interaction with mineral surfaces. In this work, we will present an integrated methodology based on First Principles methods to characterize the surface properties (structural, energetic and electronic) and the adsorption of hydrocarbons and functionalized (hydroxylated, sulphonic acid and pegylated) SiO$_2$ nanoparticles within mineral surfaces (Carbonate and Silicates). The simulations were based on the Density Functional Theory (DFT) with solid state Nuclear Magnetic Resonance calculations (1) and simulation of noncontact Atomic Force Microscopy (nc-AFM) (2) including van der Waals corrections (3). It was possible to assign the peaks in the NMR spectra for all structures studied and determine the force distance models based on simulated AFM. Our results show a chemical shift differentiation for atoms located on different sites (bulk and surface) for calcite and silicate systems as well as the differences on force versus distance curves. Interestingly, the presence of hydrocarbon molecules also modifies the chemical shift of adsorbed the Ca and Si sites with respect to the pristine and isolated surfaces. Calculated AFM forces allow us the differentiation between the different chemical sites and a clear understanding of the adsorption processes. Within the combining theoretical AFM and NMR simulations with DFT with van der Waals, it should be possible to elucidate the coordination environment of chemical species in many important complex materials in the context of geochemical phenomena.

Strata-specific bacterial diversity in aquifers of the Thuringian Basin/Germany

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The INFLUINS (Integrated fluid dynamics in sedimentary basins) project investigates coupled dynamics of near surface and deep flow patterns of fluids, transported materials and component substances in the Thuringian Basin. The extensive basin landscape is located in eastern Germany and belongs to the Triassic period of Bunter sandstone (Buntsandstein), shell limestone (Muschelkalk) and Keuper, which crop out at the surface. Older sediments and Permian (Zechstein) can be found at the edges of the basin.

With microbial investigations, we are analyzing the bacterial diversity of groundwater at different locations to see whether there are special patterns in bacterial distributions originating from the different rock strata. Furthermore, we are interested in the bacterial diversity of drilling cores and salt formations from the same locations. This will facilitate understanding fluid movement in the Thuringian Basin. We determined bacterial community from water samples out of nine natural springs and sixteen groundwater wells by cultivation and subsequent morphological, physiological and molecular identification.

First results show that the largest proportions were found to be members of Bacilli and gamma proteobacteria, including the genera *Pseudomonas*, *Marinomonas*, *Bacillus*, *Marinobacter* and *Pseudoalteromonas*.

Next steps will be a comparison of cultivation-dependent and cultivation-independent methods to gain further information on bacterial strains which were uncultivable or suppressed by other bacteria strains.

Experimental Calibration of a Garnet-Clinopyroxene Geobarometer for Mantle Eclogites

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We present a geobarometer applicable to eclogitic mantle xenoliths based on the exchange reaction involving the incorporation of Al in 4-fold coordination present as Ca-Tschermak in omphacitic clinopyroxene coexisting with garnet solid solutions. The barometer is calibrated with piston cylinder and multi-anvil experiments between pressures of 3 to 7 GPa and temperatures from 1200 to 1542 °C. Starting materials are synthetic mixtures of varying basalt compositions (hydrous N-MORB), yielding a homogeneous bimineralic garnet-clinopyroxene phase assemblage. We expand our own data set by implementing additional experimental studies conducted in eclogitic systems granting the applicability to a wider range of eclogitic compositions. All experiments are buffered in terms of Al with garnet as the Al-bearing phase. Our calibration reproduces the experimental pressures with 0.4 GPa within the 95% confidence interval. The barometer was then tested with natural eclogites from various mantle xenolith locations covering a wide P-T-X regime. The herein presented barometer opens up the possibility to determine pressures of formation for bimineralic eclogitic xenoliths without requiring additional accessory phases. With this barometer we provide an additional tool to investigate the P-T state of upper mantle heterogeneities.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Organic carbon export in Taiwan: insights from marine sediments

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Terrestrial organic C (OC) delivered to the ocean by rivers is a mix of recent OC and fossil OC derived from erosion of rocks. Burial of fossil OC in marine sediments is a simple recycling of reduced carbon and has no effect on atmospheric CO2 and O2 levels. Conversely, its oxidation consumes atmospheric O2 and returns CO2 to the atmosphere. In large-scale erosion systems (Himalaya), only graphite resists to oxidation during river transport and/or transient storage in floodplains. In contrast, disordered fossil OC observed in mountainous bedrocks and mountain rivers disappear during transport in large rivers, and are not observed in marine sediments [1]. In addition, such large scale systems may act like a CO2 pump as a huge amount of modern OC is delivered and buried in the Bengal Fan marine sediments [2].

Here, we investigate the isotopic composition (14C, 13C), organic geochemistry and structure (Raman spectroscopy) of OC in recent turbidite deposits all around Taiwan. We show that the bulk OC is primarily composed by terrestrial modern and fossil OC, but also includes marine OC. We discuss the geochemistry of OC in marine sediments with respect to the modern and fossil OC sources on the Taiwan island. We quantify the respective contributions of these three end-members to the total OC, and discuss the sediments provenance based on the structure and geochemistry of fossil OC. Comparison of the OC in marine sediments with data existing for Taiwanese rivers [3] allows for discussing the carbon budget of erosion. In particular, unlike large-scale systems, fossil OC is massively transferred to marine sediments during erosion in Taiwan. Globally, such small-scale systems with very active erosion and short transfer to the ocean may act as an important sink for OC in the long-term carbon cycle.


Assimilation of sediments embedded in the oceanic arc crust: myth or reality?

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Volcanic products from oceanic arcs afford a unique opportunity to study the subduction factory. Although most of these products are not primitive, the impact of assimilation of the arc crust is often ignored with the consequence that trace element and isotopic compositions are commonly attributed only to varying contributions from different source components. This jeopardises the integrity of recycling mass balance calculations. Here we use Sr and O isotope mineral data from a suite of volcanic rocks from the Lesser Antilles arc to show that assimilation can be significant in oceanic arc basement. Analysis of 87Sr/86Sr in single plagioclase phenocrysts from the Soufrière Volcanic Complex (St Lucia) reveal isotopic heterogeneity within and among hand samples ranging from 0.7083 to 0.7094. δ18O measurements show extreme variation beyond the mantle range: up to +10.9‰ for plagioclase, +11.8‰ for quartz, +9.8‰ for amphibole and +9.5‰ for pyroxene. Such 87Sr/86Sr isotope disequilibrium and extreme δ18O values strongly argue for assimilation of material located within the arc crust. A positive correlation between mineral δ18O and the whole rock radiogenic isotopes shows that assimilation seems to be responsible for the isotopic heterogeneity observed in St Lucia but also in the whole Lesser Antilles since St Lucia covers almost the whole-arc range of isotopic composition. This highlights the need for detailed mineral-scale investigation of oceanic arcs suites to quantify differentiation that could lead to misinterpretation of source composition and subduction processes.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Constraining the Thermal History of an Ultra-hot Orogen from Metamorphic Reaction History and Garnet-Orthopyroxene Diffusion Modelling Studies

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The southern margin of the Central Indian Tectonic Zone experienced a history of metamorphism at different sets of conditions during the Proterozoic. A primary, high temperature assemblage of aluminous orthopyroxene ($X_{\text{Mg}} = 0.585$) + calcic plagioclase ($\text{An}_{49-52}$) + magnesian ilmenite ($X_{\text{MgTiO}_3} = 0.06-0.07$) experienced three recrystallization events ($M_1$ with a $T_{\text{Max}}$ of $\sim$1000 °C at 9.5 kbar and $M_2$ at 900°C, 6.7 kbar and $M_3$ at 770°C, 7.5 kbar) to produce two generations of garnet, orthopyroxene and biotite. We have integrated observations on metamorphic reaction textures, mineral compositional zonation, calculated pseudosections, available geochronological data, and diffusion modelling of compositional profiles in garnet and orthopyroxene to constrain the timescale of thermal evolution for this complex sequence. We find that at least a three stage thermal history is necessary to account for all observations consistently. Cooling rates on the order of 10’s of °C/ my indicate that high temperatures of $M_1$–3 metamorphism were sustained for tens of million years, providing evidence of a long lasting (i.e. > 60 my) regional metamorphic event.

The origins of detrital clays on the East China Sea shelf

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There are two kinds of sediment source-to-sink (S2S) systems on the East China Sea shelf. One is “large river/delta – wide shelf – huge input – slower sediment transfer – strong anthropogenic impact” represented by the Changjiang (Yangtze) River; another is “mountainous river – narrow shelf – huge input – rapid sediment transfer – extreme climate event” represented by the rivers in Taiwan Island. To study the contributions of these two S2S systems to clayey sediments accumulated on the shelf, a total of 66 clay samples were selected from the shelf, the Changjiang and mountainous rivers entering the East China Sea. A multivariate analysis technique (EOF) was used to process elemental geochemical data.

The covariance between elements explained by the first two eigenmodes is about 76%. The first mode can explain about 62% of the data variability, in which elements are divided into two groups according to the sign of their eigenvectors. One group is dominated by Ca, Fe, Mg, Mn, P, Co and another by Al, Si, K, Na, Ti and REE. We interpret Mode 1 to be different clay mineral assemblages in the source areas. The second mode can explain about 14% of the data variability. One group consists of K, Na, Rb and LREE while the other elements belong to another group. Mode 2 probably indicates the proportion of non-clay minerals in the clay sediments. Based on the corresponding eigenweights of each sample, the spatial distribution patterns of the clays were revealed. The clay from the Changjiang River was primarily transported southeastward and formed an inner shelf mud belt that mixes with the Taiwan-derived clays in northern Taiwan Strait. Some clay from the Changjiang River may disperse eastward and mix with the clay sourced from the old Yellow River delta in the southwestern Yellow Sea. The oceanic circulation in the East China Sea predominately controls the dispersal and deposition of detrital clays on the shelf.

Acknowledgements: This work was supported by NSFC research fund (Grant No: 41076018, 41225020).

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Enhanced stability and inhibited dissolution of uraninite by nanoparticulate iron sulfide under oxic conditions

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Redox transition of uranium from dissolved U(VI) species to insoluble U(IV) precipitates can result in successful sequestration of uranium in contaminated soils and sediments. Recent studies have shown that naturally-occurring mackinawite (FeS) can provide an electron source for U(VI) reduction and retard uraninite reoxidation upon oxygen intrusion[1]. However, few studies have provided mechanistic and kinetic information on the interactions of uraninite with FeS solid under oxic conditions. The present study investigated the mechanism(s) and reaction kinetics of inhibited U(IV) reoxidation and transport by nanoparticulate FeS. The oxidative dissolution of uraninite by dissolved oxygen (DO) in FeS-bearing groundwater were conducted using batch and flow-through reactors as a function of pH, FeS content, DO and calcium concentrations, to assess the impact of critical geochemical factors on UO₂ dissolution kinetics. The results indicated that the dissolution rate of UO₂ decreased by an order of magnitude when FeS was present relative to control. The rate decreased rapidly with decreasing DO levels and increasing FeS content. In the presence of Ca²⁺, the rate was even lowered owing to the formation of Ca-containing passivation layer on uraninite surfaces. Until the depletion of FeS, DO concentration remained at significantly low levels, suggesting FeS was an effective oxygen scavenger. During the inhibition period, dissolved Fe(II), Fe(III) hydroxides, and elemental sulfur were produced from FeS oxidation. In contrast, uraninite remained as U(IV) solid as verified by X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). Although dissolved Fe(II) was not shown to reduce U(IV) under oxic conditions, residue FeS particles was responsible for inhibiting UO₂ dissolution by reducing soluble U(VI). This study suggests that naturally-occurring FeS may serve as an oxygen scavenger and a U(VI) reductant for effective uranium sequestration. These findings have direct implications for our understanding of uraninite redox transition and long-term stability in the subsurface.

[1] Bargar et al. (2013), PNAS

The Mesozoic dolomites of the Levant margin - evaluating dolomitization style and mechanism from configuration and stable isotope geochemistry

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The record of the Levantine margin provides a unique window into dolomitization through the Mesozoic [1] and dolomitization in general. Ample carbonate sediments have accumulated through the Triassic, Jurassic and Cretaceous in this region, maintained at relatively shallow burial depth [2], and currently exposed at the surface. We examined the depositional configuration, and the geochemical and stable isotope compositions across several limestone-dolostone transitions, with the intention of inferring the paleoenvironmental trends leading to these transitions and the style of dolomitization in these rocks.

Sequences where selected based on the presence of repeated interchanges between limestone and dolostone, in settings where the occurrence of the dolomite is likely to be derived from early diagenetic processes and interaction with marine or evaporated marine water. Three different settings were targeted: i) sub-tidal, open marine, evaporite-free (Cretaceous), ii) intertidal, open marine, evaporite-free (Jurassic), and iii) restricted lagoon, in association with sulphate evaporites (Triassic). In each case, a cross-section was sampled at a spatial resolution of about 50 cm to evaluate lithological changes and variability in stable isotope ratios. Following the identification of transitions of interest, these were sampled at a spatial resolution of 1-3 cm.

Mineralogy and Ca to Mg ratios in the carbonates were determined by X-ray diffractometry, and the isotopic ratios of carbon and oxygen (δ¹³C and δ¹⁸O) were measured by mass spectrometry. Sedimentary textures were investigated in hand samples and in some cases by petrographic microscopy. The results of these analyses will be presented and their implications for mechanisms of dolomite genesis discussed. Future work will include analysis of Ca and Mg isotope ratios in the samples to further illuminate dolomitization mechanisms.

**Links between diel vertical migrations and ocean oxygen**

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Diel vertical migration of zooplankton and micronekton - the largest migration on Earth, is a major but poorly quantified component of the ocean’s biological pump. The impact of this migration on oceanic oxygen has received relatively little attention, partly due to the lack of a predictive framework. By using a global synthesis of acoustic data we show that diel vertical migrations are characterized by coherent large-scale patterns, which are strongly correlated with the distribution of subsurface oxygen. Open ocean oxygen minima, when present, emerge as potential refuges for vertical migrators. Including a representation of the respiratory needs of migrating populations in a three-dimensional ocean model suggests that, by focusing respiration in poorly-ventilated regions of the upper ocean, diel vertical migrations intensify oxygen depletion at the upper margin of oxygen minimum zones. This coupling between migrating animals and marine oxygen may have important implications for fisheries and oxygen minimum zone chemistry in a changing ocean.

**The river Po: geochemical fluxes and related insights on weathering processes and erosion rates**

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The Alps and the Apennines both convey water and sediments to the Po river that is the most important fluvial system of the Italian Peninsula, characterized by a length of 650 Km, an hydrological basin of 74000 km² and an average discharge of 47 Km³/yr. Major and trace elements, stable isotope composition of water and radiogenic strontium isotopes were used to characterize the sources and fluxes of solutes. Compared with the local meteoric isotopic signature, stable isotopes (δ¹⁸O between -10.8 and -9.2; δD between -70.0 and -65.4) reveal that most of the recharge occurs in the north-western part of the basin, i.e. conveyed mainly from the highlands. Although subordinate, carbonatic lithologies are preferentially involved in the weathering processes inducing the typical Ca-HCO₃ hydrochemical facies and a specific strontium isotopic signature (87Sr/86Sr 0.7090-0.7092) that is intermediate between that of Mesozoic carbonates (0.707-0.708) and felsic igneous and metamorphic rocks (> 0.701). The data also provide insights on the erosion and denudation rates of the orogens bordering the basin. The observed TDS (average and median of 39 measurements are 268 and 292 mg/l, respectively) suggest that a solute flux in the order of 13*10⁶ t/yr is transferred from the Po River toward the Adriatic Sea. A total erosion of 68*10⁶ t/yr is estimated within the Po River drainage basin, assuming that solute represent a fraction (of ca 20%) of the weathering products. This estimation conforms to other recent investigations [1].

CO₂ Dissolution rates during CO₂ injection: a consequence and measure of reservoir heterogeneities

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CO₂ dissolution during and after injection into geological storage sites is potentially an important mechanism for stabilising and securing the storage but may lead to enhanced fluid-mineral reactions with both positive and negative consequences for the security of storage. Important questions are how does reservoir heterogeneity influence CO₂ dissolution rates and does the tendency of the low-viscosity CO₂ to finger during injection increase dissolution rates? Here we evaluate the rates of possible CO₂ dissolution in an injection setting by simple pseudo-1D flow modelling with diffusion in the orthogonal direction and compare this with numerical modelling of flow and diffusion in 2D. The results show that the magnitude of CO₂ dissolved is strongly controlled by the rapid flow of brines determined by reservoir heterogeneities. The consequences for fluid-mineral reactions are that these may be strongly localised and this could have important implications for feedbacks between flow and permeability changes in reservoirs.

The results are tested against an injection experiment which utilised CO₂ injection for enhanced oil recovery (EOR) in a ~5,000 m deep Pieve Santo Stefano 1 (PSS1) borehole located in the Upper Tiber Basin (Northern Apennines, Italy) and (ii) natural gas discharges located in the surrounding of the Mt. Fungaia ophiolitic-bearing complex (Ligurian Units), are presented and discussed.

Fluid geochemistry of the deep CO₂-rich Caprese Reservoir (Northern Apennines, Italy)

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The chemical and isotopic composition of (i) CO₂-rich fluids exploited from Caprese Reservoir (CR) by the ~5,000 m deep Pieve Santo Stefano 1 (PSS1) borehole located in the Upper Tiber Basin (Northern Apennines, Italy) and (ii) natural gas discharges located in the surrounding of the Mt. Fungaia ophiolitic-bearing complex (Ligurian Units), are presented and discussed.

The CR fluids are hosted in fractured dolostones layers of Burano Fm. [1] and consist of CO₂-, N₂-rich gas phase and saline (~82 g/L) NaCl brine. The δ¹³C-CO₂ and δ¹⁵N-N₂ values are interpreted as produced by mixing of deep fluids originated by mantle degassing and thermometamorphic processes involving Mesozoic limestones. Water isotopes and ³H values indicate that the CR brine is recharged by a long (>50 yr) hydrologic circuit fed by meteoric precipitations.

The naturally discharging gases from the study area are fed by CR, likely due to the fact that the steep Arbia Val Marecchia Line transverse tectonic elements provide preferential paths for these deep-seated fluids, favoring their uprising up to the surface gas vents [2]. The interaction of the ascending CR gas with ophiolite-bearing Ligurian Units and Cervarola-Falterona Unit produces secondary H₂, H₂S and light hydrocarbons in Mt. Fungaia gases.

Precise U–Pb zircon CA-ID-TIMS ages and Sr isotopes for the Plana pluton, Srednogorie, Bulgaria

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We report new, high precision CA-ID-TIMS U–Pb single zircon ages for the Plana pluton, a part of the ABTS belt in SE Europe. The pluton is located at the Central Srednogorie-Rhodopes border, ~60km SE of Sofia. in situ differentiation of high potassium calc alkaline magmas produced gradually varying rock compositions [1]. We analyzed a granite from the central parts of the pluton (A); and a monzogabbro-diorite from the periphery of the pluton (B).

The three youngest grains in (A) overlap and yield a weighted mean 206Pb/238U age of 77.87±0.07 Ma (2σ, MSWD=1.01), our best estimate for the crystallization age of the granite. Two zircons, interpreted as antecrysts, are concordant at ~78 Ma. The remaining two grains, interpreted as xenocrysts, are concordant at ~440 Ma. In (B), two of five grains are concordant at ~440 Ma; the remaining three zircons are discordant and older. Ages of ~440 Ma, are also reported for inherited zircons in other Upper Cretaceous intrusives and Variscan granitoids from Central and Eastern Srednogorie [2, 3, 4]. The presence of inherited zircons provides direct evidence for wall-rock assimilation.

Comparison of our data with published U–Pb ages [3, 5] suggests that the Plana pluton crystallized in the late stages of Upper Cretaceous magmatism in Srednogorie. Initial Sr isotopes of seven studied rocks are between 0.7043 and 0.7050, within the range of the least radiogenic Upper Cretaceous magmatism in Srednogorie. Studies from Central Srednogorie show a trend toward younger and more mantle-influenced magmatism from north to south [5]. Our high precision 77.87 Ma age, and the mantle-dominated Sr isotope signature of the rocks, correlate the Plana pluton with the magmatic activity of southern Central Srednogorie. We thank Momchil Dyalgerov and Svatoslav Georgiev for analytical help, and Judy Hannah and Holly Stein for support.

Colloidal properties of biomineralized nanoselenium: implications for bioremediation, resource recovery and environmental transport

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Microbial selenium (Se) bioremediation is based on conversion of water soluble, toxic Se oxyanions to water insoluble, biogenic pure elemental Se of particle sizes in the nanometer range (bioNSe). The colloidal stability of the bioNSe suspensions hamper a straightforward removal and recovery by gravitational settling. BioNSe that is not removed from suspension may leave bioremediation reactors with the effluent and is subject to transport and re-oxidation to the original toxic oxyanions. For the first time, colloidal stability fields of pure bioNPSe were determined by electrophoretic mobility (ζ-potential) measurements and column settling experiments (ICP-MS). It was demonstrated that circumneutral pH, commonly applied in bioremediation, prevents settling of bioNPSe, since the particles are strongly negatively charged. Counter cations and protons were used to screen efficiently this intrinsic negative charge. In this manner, settling could be significantly accelerated (up to 86.2 ± 3.5% within 0.5 h) at cation concentrations that would only increase overall treatment costs to minor extents. The ζ-potential measurements showed furthermore, that significantly dissimilar transport behaviour is to be expected in different natural waters (salt, dissolved organic matter rich), which can result in accumulation of Se in certain environments, if bioNPSe leaves bioremediation reactors.

Opening the foraminiferal proxy black box a bit further

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Even though our geochemical proxy toolbox is ever increasing and our analytical techniques are getting more sophisticated, our fidelity at reading past ocean climate information has only slightly improved. This is mainly due to the fact that most relationships are still empirical and controlled by more than just the target parameter. The outstanding challenge is to open the black box and develop a mechanistic understanding of proxy incorporation and preservation. We have carried out a whole suite of laboratory experiments to better understand the calcification processes and the pathways of Mg, Sr, Ba, U and B using confocal laser microscopy, TEM, AFM and simultaneous analyses of B/Ca and $^{11}$B using femtosecond laser ablation and MC-ICP-MS.

Together, the results show a high degree of biological control during calcification and proxy incorporation. We have used the benthic foraminifers *Ammonia aomoriensis*, *Amphistegina lessonii*, *Heterostegina depressa* and the planktonic foraminifer *Orbulina universa*. Lessons learned and a tentative model will be presented.

Experimental constraints on Fe isotope fractionation in fluid-melt-oxide-sulfide assemblages

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We report the first experimental data that quantify directly the effect of a fluid phase on stable iron isotope fractionation at magmatic conditions. Our investigation was stimulated by the hypothesis that degassing causes the heavy iron isotope signature measured in degassed rhyolites [1,2], but published experimental studies of iron isotope fractionation lacked a fluid phase.

We used a rhyolite melt, NaCl-bearing aqueous fluid, and magnetite or pyrrhotite. Charges were run at 400, 600, or 800°C, 150 MPa for mineral–fluid, and 800°C and 100 MPa for mineral–melt–fluid; fO2 was buffered at ~NNO. Isotopic compositions of starting and quenched phases were obtained by MC-ICP-MS. Time-series runs and the three-isotope method were used to assess equilibrium.

Our data indicate that rhyolite melt at 800°C is isotopically lighter than co-existing fluid ($\delta_{\text{melt-fluid}} \approx -0.20 \pm 0.07$‰). Magnetite behaves as predicted ($\delta_{\text{fluid-magnetite}} \approx +0.75 \pm 0.07$‰ at 800°C), becoming isotopically heavier relative to both fluid and melt. An andesite-fluid experiment (FMQ+0.5, 1000°C, 150 MPa) yielded an isotopically lighter melt relative to the starting glass, consistent with the coexisting fluid being isotopically heavier than andesite melt. These data suggest that fluid exsolution from silica-rich melts is not the cause for the increased $^{56}$Fe/$^{54}$Fe ratio in degassed rhyolites. Interestingly, magmatic and hydrothermal magnetite show distinct iron isotope signatures, suggesting that the iron isotope values of minerals deposited by these processes may serve as geochemical fingerprints of the source reservoir for iron. Additional data from sulfide runs support the observation that individual minerals can fractionate iron differently and that pyrrhotite preferentially incorporates $^{54}$Fe into its structure ($\delta_{\text{melt-pyrrhotite}} \approx -0.75 \pm 0.01$‰ at 800°C).

These data corroborate the hypotheses that both fluid exsolution and crystal fractionation could influence the isotopic composition of a melt, but perhaps not as predicted. Owing to the importance of melt degassing as a critical process for the formation of ore deposits, our data may also help resolve debates regarding the origin of deposits that may have formed by either magmatic or hydrothermal processes.

Magmas going through Icelandic crustal filter

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Eruption of large-volume basalts in large igneous provinces and hotspots occurs throughout areas of preexisting thick crust and crust overloaded by early eruptions from the same plume. Iceland represents a good testing ground for estimating the amounts of upper crustal contamination of mantle-derived magma in long-lived propagating rifts - magmatic pipelines going through the isotopically fingerprinted low-δ18O thick crust affected by rain and glacial meltwaters. We report analyses of individual primitive olivines across Iceland and demonstrate that the Icelandic plume is not severely depleted in δ18O neither contains higher than mantle values (5.2-4.6‰ for Ol >Fo86). We observe a positive correlation of Fo and δ18O(olivine) down to Fo75 suggesting that crustal differentiation and assimilation is responsible for low-δ18O evolved olivines and host basalts. We report new data and interpretation of oxygen isotope diversity in olivines from large volume rift basaltic eruptions and investigate in detail olivine-basalt oxygen isotopic equilibria. Up to 3‰ variations of Fo75 to Fo86 olivines suggest rapid transformation of mantle-derived magmas in the magma plumbing systems. Low-δ18O values of large volume basalts (e.g. Laki, Veidivotn), with MgO <5wt%, require that tens of percent of a low-δ18O mafic component was added to normal-δ18O mantle derived basalt. Only limited δ18O whole rock heterogeneity is present in large volume basalts suggesting effective mixing and homogenization prior to eruption. Diffusive reequilibration of disequilibrium olivines and plagioclase require hundreds of years, and their longest residence is in the semi-frozen cumulates underneath volcanoes. Rapid transport along a bifurcating network of dikes and sills inside of the hyaloclastitic upper crust provide a viable mechanism for crystal entrainment and basalt mixing by forced convection. We provide a simple numerical model of this process. We further discuss the effect of flowing basalt in upper crustal lithologies leading to crustal melting and generation of low-δ18O silicic melts with heterogeneous crystal cargos.

Rhyolites-Hard to Produce, Easy to Recycle: Isotopic diversity in zircons as petrogenetic tool

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Rapid pace of discovery of oxygen isotope diversity in zircons and other minerals in large volume ignimbrites worldwide suggests that this phenomenon characterize many silicic units studied so far by in situ methods. We report new results from calderas in the Snake River Plain: Picabo, early Bruneau, in addition to previously reported Yellowstone and Heise), Kamchatka, and rhyolites from rifts of Iceland (Askja, Hekla, Torfajökull). As low-δ18O oxygen values fingerprint petrogenesis to the upper crust, these observations lead to a model of silicic magma by "double-recycling" of zircon-saturated, silicic to intermediate rocks. Initial melts are produced slowly in diverse batches and the isotopic signature of zircons record their immediate environment of growth. Next, magma batches with diverse zircons merge into larger-volume magma bodies, which mix crystals together and erupt quickly. Concave-up crystal size distributions of zircons and quartz in studied voluminous ignimbrites can be explained by just two episodes of reprecipitation. Following the melting simulation of [1] we use visco-plastic rheology for surrounding rocks to explain the formation of magma batches generated side by side and merging them together. We observe: 1) Fast convective melting with low heat dissipation. 2) Efficient mixing on large (kilometers) horizontal scales, due to the vigorous flow field induced by compositional convective melting of silicic predecessors by superheated rhyolites. Chaotic, meter-scale vortexes of altering directions cause disintegration of the liquid parcels to diminishing size. The marker method allows us to track particle mixing (i.e., how zircons with diverse isotopic values brought together). 3) Mechanical interaction of the closely-spaced sills in hot visco-plastic upper crust with low yield stress (<100 MPas) leads to mechanical failure (both brittle and plastic) of separating screens leading to the coalescence of sills into a single body. We suggest that analogous processes of rapid two-stage segregation may characterize granitic batholith, and large supervolcanic magma bodies formed by remelting.

Space-Time Kriging of Precipitation Reconstructed at 12-km Grid Intervals from Tree-Ring Records

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Understanding and preparing for future hydroclimatic variability greatly benefits from long (i.e., multi-century) records at seasonal to annual time steps that have been gridded at km-scale spatial intervals over a geographic region. Kriging is a geostatistical technique commonly used for optimal interpolation of environmental data, and space-time geostatistical models can improve kriging estimates when long temporal sequences of observations exist at relatively few points on the landscape. Here I present how a network of 22 tree-ring chronologies from single-leaf pinyon (Pinus monophylla) in the central Great Basin of North America was used to extend hydroclimatic records both temporally and spatially. First, the Line of Organic Correlation (LOC) method was used to reconstruct October-May total precipitation anomalies at each tree-ring site, as these ecotonal environments at the lower forest border are typically moisture limited. Individual site reconstructions were then combined using a hierarchical model of spatio-temporal kriging that produced annual anomaly maps on a 12x12 km grid during the period in common among all chronologies (1650-1976). Hydro-climatic episodes were numerically identified and modeled using their duration, magnitude, and peak. Spatial patterns were more variable during wet years than during dry years, and the evolution of drought episodes over space and time could be visualized and quantified. The most remarkable episode in the entire reconstruction was the early 1900s pluvial, followed by the late 1800s drought. The 1930s ‘Dust Bowl’ drought was among the top ten hydroclimatic episodes in the past few centuries. These results directly address the needs of water and natural resource managers with respect to planning for ‘worst case’ scenarios of drought duration and magnitude at the watershed level.

The absolute Cr isotopic ratios of the components of carbonaceous chondrites

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Non linear isotopic anomalies are common for Cr in carbonaceous chondrites at the mineral scale where percent level variations are common for 54Cr [1,2]. When these anomalies are small relative to the dispersion of mass discrimination during TIMS measurements, the identity of the anomalous isotope(s) is not unambiguous. For the stepwise dissolution fraction of C1 and C2 carbonaceous chondrites former experiments designate 54Cr as the major varying isotope and 53Cr as varying only according to 53Mn decay. Nevertheless below about 10 δ variations some effects can still be present on the two normalizing isotopes 52Cr and 50Cr. As evaporation and condensation in the forming solar system is a credible possibility, significant fractionation can also be present between the components that constitute carbonaceous chondrites. We address this issue in this presentation.

In Orgueil, Tagish Lake, Tafassasset and Paris, dissolution fractions in which non-mass-dependent 54Cr effects can spread up to close to 2% [1-3] were investigated. A Neptune MC-ICPMS was used in the medium resolution mode (M/ΔM~5000) to avoid interferences from Ar compounds in the Cr mass range. 54Cr/52Cr ratios are measured within a 0.05 δ (permil deviation relative to NIST 979). Radiogenic contributions on 53Cr can be substracted using the TIMS data obtained on the same Cr fractions.

54Cr/52Cr ratios in fractions from stepwise dissolution in C1 and C2 chondrites [1-3] are identical to their respective whole rocks within 0.1 δ. This implies that despite large differences in 54Cr the other three isotope: 56Cr, 52Cr and 53Cr are initially in identical proportions in all the mineral fractions investigated with the present procedure. At present, carbonaceous chondrites seem to contain only two primordial Cr isotopic components: one with normal 50Cr, 52Cr, 53Cr and a deficit in 54Cr, and a second one which consists of pure 54Cr. Data on new, recently found carbonaceous chondrites will also be presented [4].

Protracted cooling from Neoproterozoic metamorphic events in the NW Highlands, Scotland investigated using garnet Lu-Hf and Sm-Nd geochronology

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The Moine Supergroup of the Northern Highland Terrane in Scotland records several orogenic events. The earliest of these is the Knoydartian (830-740 Ma). All previously published evidence for this event comes from West Inverness-shire. Lu-Hf and Sm-Nd garnet geochronology records much more widespread Neoproterozoic metamorphism, with evidence from Shetland to Mull. This data also shows that the Morar Group has been affected by the Renlandian event of the Valhalla Orogen. It also demonstrates that the younger limit of Morar Group deposition is older than previously thought (>950 Ma).

All of the samples all record a systematic difference between the Lu-Hf and Sm-Nd ages, the Sm-Nd ages being 10-20% younger than the Lu-Hf ones. Garnet cores and rims have been dated using Lu-Hf and Sm-Nd and the difference between the cores and rims is the same for both isotopic systems. This suggests that the difference between Sm-Nd and Lu-Hf is due to the difference in closure temperatures. One exception gives Lu-Hf and Sm-Nd ages which are within error and could suggest that this sample records garnet growth in both isotopic systems or relates to very fast cooling.

Iron Oxidation and Reverse Electron Flow In a Photoferrotroph

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Biological iron oxidation is of interest to geobiologists as an oxygen independent mechanism of ferric iron production. *Rhodopseudomonas palustris* TIE-1 is a versatile purple phototroph with the ability to grow using ferrous iron (Fe(II)) as the sole electron donor. Previous studies showed that the pio operon, encoding an outer membrane porin, a decaheme cytochrome, and a high potential iron protein (HiPIP), are vital to Fe(II) oxidation. This work further explores the iron oxidation pathway through in vitro characterization of the HiPIP and in vivo visualization of photosynthetic electron transport with flash induced absorbance spectrometry. In vitro studies showed that the HiPIP can donate electrons to the reaction center at a rate much slower that that found in energy generation. Our in vivo studies, however, show that antimycin (a bc1 complex inhibitor) blocks reduction of the quinone pool by Fe(II), indicating that electrons may reduce the quinone pool of the cell through the bc1 complex instead of through the reaction center as previously thought. We have also found that the quinone pool of *R. palustris* TIE-1 is reduced by Fe(II) over short time scales even in mutants lacking the pio genes, although the precise rates of this reaction were not determined. These results indicate that the mechanisms of iron oxidation are more complex than originally thought, and that the path electrons take from Fe(II) to carbon reduction is similar to the pathway found in acidophillic Fe(II) oxidation.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Crystallization kinetics of apatite nanocrystals from amorphous calcium phosphate in water by in situ synchrotron powder diffraction

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Crystallization of minerals from amorphous precursor phases is emerging as a major pathway for crystallization in several systems but remains poorly understood. Here we use in situ X-ray diffraction to study the crystallization kinetics of nanocrystalline apatite from amorphous calcium phosphate in water. We find a striking dependence of crystallization behavior on whether K+ or Na+ is used as counter ion.

In situ X-ray diffraction experiments were performed with ~10 s time resolution [1, 2, 3]. The data were analyzed by Rietveld refinement procedures determining the nanocrystal size, the amount of crystalline material present, the lattice constants, and the background [1, 2]. The amorphous precursor phase was clearly observed in the first time points [2] and was gradually replaced by the nanocrystal diffraction pattern of the forming apatite phase.

The crystals were found to be formed as almost spherical crystallites that soon after formation started growing preferentially in the c-axis direction of the hexagonal apatite crystals giving needle-shaped nanocrystals. This rapid anisotropic growth was followed by an Ostwald ripening stage, with slower crystallite size growth rates. During this stage, growth was preferentially perpendicular to the c-axis slightly lowering the shape anisotropy.

Using K+ instead of Na+ as counter ion resulted in drastic changes in growth kinetics. Sodium allows the incorporation of dissolved carbonate into the forming apatite while potassium does not. This difference led to more rapid crystallization for sodium as a counter ion and resulted in crystallites with different sizes and size anisotropies.

The present work provides detailed insights into how anisotropic crystal morphologies develop and shows that seemingly innocent changes in environment, such as choice of counter ions may have profound impacts on crystallization behavior.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org

Origin of porphyries related to Cu-Mo mineralization, California-Vetas district, Colombia

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Porphyry Mo- Cu mineralization in the California-Vetas district, Eastern Cordillera, Colombia is coeval with 10.9 - 8.4 Ma granodiorite porphyry stocks and overprinted by epithermal Au-Ag mineralization. Mineralization is hosted by Grenvillian-aged paragneisses (Bucaramanga Gneiss) and Late Triassic to Early Jurassic peraluminous granites with > 70% SiO2 and metaluminous diorites with SiO2 54.9 - 60.4 wt%.

Late Miocene rocks are weakly peraluminous granodiorite porphyries with SiO2 61- 67%, sharing some characteristics with adakite-like rocks widely associated with porphyry mineralization elsewhere in the Andes. Although Miocene rocks do not have low Y (<15 ppm) or depleted HREE, they have high Ba (930-1500 ppm), high Ba/La (28 to 50), high Sr (850 to 1100 ppm), high Sr/Y (50-78) only minor Eu anomalies and depleted MREE compared to the Mesozoic granites (400-700 ppm Ba; Ba/La 14-25; 80-150 ppm Sr; Sr/Y 2.5-14), and diorites (900 -1200 ppm Ba; Ba/La 20-32; 619-750 ppm Sr; Sr/Y 22-25). Their initial 87Sr/86Sr is less radiogenic than Neogene Caribbean sediments, precluding a sedimentary source for the high Sr and Ba. Instead, a fluid source from serpentinized lithospheric mantle, fluxing the overlying subducted oceanic crust and mantle wedge is suggested. The geochemical signal may have been enhanced by the overlapping subducting Nazca and proto-Caribbean slabs at depth.
Estimating the role of competing ions on the arsenic mobilization processes in the aquifers of Bengal basin by surface complexation modeling


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This study investigates the relative roles of the different competing ions on the arsenic (As) mobilization in the sedimentary aquifers of Bengal basin by surface complexation modeling of the temporal variability of As in shallow (<50 m) groundwater. Two sets of piezometers (2 × 5 = 10), installed at the two sites with relatively contrasting dissolved As concentration in groundwater, were monitored bi-weekly for As and other hydrogeochemical parameters over a period of 20 months. The estimation of the standard deviation (SD) for As(III) reflects strong temporal variation (SD 910 µg/L) in all the piezometers of two sites over the monitoring period. Particularly, the variation is more prominent in the shallowest part of the aquifer, where the site specific cyclic trends are evident. While, As(V) shows significant temporal variation in the piezometers of high As site only and no specific trend is reflected in the variation.

Two different surface complexation models (SCMs), developed for ferrihydrite and goethite have been explored to account for the observed temporal variation in As(III) and As(V) concentrations. The SCM for ferrihydrite has provided the better estimation for both As(III) and As(V) variations. Among the different competing ions, PO4 3- appears as the major competitor of As(III) and As(V) adsorption onto ferrihydrite and the competition ability decreases in the order PO4 3- >> Fe(II) > H4SiO4 = HCO3-. It is further revealed that a small decrease in pH significantly increases the concentration of As(III) and decreases the As(V) concentration and vice versa. The present study suggests that the reductive dissolution of Fe oxhydroxides alone cannot explain the observed high As concentration in groundwater of the sedimentary aquifers. Perhaps, the reductive dissolution of Fe oxhydroxides followed by competitive sorption reactions with the aquifer sediment is the processes conducive for As enrichment in the groundwater of Bengal basin.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
The Lu-Hf BSE parameters and the early Earth zircon record

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The long-lived $^{176}$Lu-to-$^{176}$Hf decay system is a powerful tool to understand ancient chemical fractionation events associated with planetary differentiation. Intrinsic to application of such isotopic tracers to study the early Earth is knowledge of chondritic reference values for the Lu-Hf system (bulk silicate Earth, BSE) and the precise value of the decay constant for the parent $^{176}$Lu isotope. Using a BSE estimate based on chondrite meteorites [1], detrital Hadean zircons (>3.8 Gyr) from the Jack Hills metasedimentary belt record extremely enriched Hf-isotope signals suggesting early extraction of a continental crust (>4.5 Gyr) but fail to identify a prevalent complementary depleted mantle reservoir. However, this conclusion assumes that the present-day Hf-isotope composition of bulk chondrite meteorites can be used to estimate the composition of BSE. Recent internal $^{176}$Lu-$^{176}$Hf systematics of the pristine 4564.58±0.14 Myr SAH99555 angrite [2] define a Lu-Hf age that is ~300 Myr older than the age of the solar system [3]. This confirms the existence of an energetic process yielding excess $^{176}$Hf in affected early formed solar system objects through the production of the $^{176}$Lu isomer ($t_{1/2}$=3.9 hours). This conclusion is now supported by new $^{176}$Lu-$^{176}$Hf data of eucrite meteorites [4]. This implies that chondrite meteorites contain excess $^{176}$Hf (~5-unit) and their present-day composition may not be used to infer the Lu-Hf parameters of BSE. Using a revised BSE estimate based on the SAH99555 isochron, we note that Earth’s oldest zircons preserve a record of coexisting enriched and depleted hafnium reservoirs as early as 4.3 Gyr in Earth’s history, with little evidence for the existence of continental crust prior to 4.4 Gyr. This contrasting interpretation of the early zircon record requires reassessing the validity of using chondrites to define the Lu-Hf BSE parameters. To better understand the extent of $^{176}$Hf excesses in meteorites and the solar system’s initial $^{176}$Hf/$^{177}$Hf value, we initiated a $^{176}$Lu-$^{176}$Hf study of additional quenched angrites via the internal isochron approach, including D’Orbigny, NWA 1670 and NWA 7203. Our new U-corrected Pb-Pb dates for these meteorites indicate coeval formation of NWA 7203, SAH99555 and D’Orbigny. NWA 1670 crystallized ~1 Myr earlier and, thus, is the oldest known angrite.


Sulfur isotopic evidence for sources of volatiles in Siberian Traps magmas

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We present new measurements of $\delta^{34}$S in melt inclusions from the Siberian Traps. The Siberian Traps flood basalts transferred a large mass of volatiles from the Earth’s mantle and crust to the atmosphere [1]. The eruption of the large igneous province temporally overlapped with the end-Permian mass extinction, and also generated ore deposits of major economic importance. Constraints on the sources of Siberian Traps sulfur and other volatiles are critical for determining the overall volatile budget, the role of assimilation of crustal materials, and genesis of Noril’sk massive sulfide deposits. Sulfur isotopic ratios vary among mantle and crustal materials, with characteristic mantle $\delta^{34}$S values around 0±2 ‰ with respect to Vienna Cañon Diablo Troilite (VCDT), and crustal $\delta^{34}$S values between -50 ‰ and +40 ‰. In conjunction with previously published whole rock measurements from Noril’sk [2], our sulfur isotopic data suggest that crustal assimilation was widespread and heterogeneous—though not universal—during the emplacement of the Siberian Traps. Evidence for open-system degassing implies that episodes of explosive volcanism may have been phreatomagmatic. Carbon concentrations constrain minimum entrapment depths of melt inclusions to shallow crustal depths. Magmas likely interacted with sedimentary materials depleted in $^{34}$S such as shale or coal, in addition to evaporites enriched in $^{34}$S. These crustal materials may have increased the total volatile budget of the large igneous province, thereby contributing to Permian-Triassic environmental deterioration.

Chlorite dissolution experiments under CO₂ saturated conditions

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The injection and long-term storage of supercritical CO₂ (scCO₂) into geological reservoirs is seen as an important option to mitigate rising levels of atmospheric CO₂. Predicting what changes take place to geochemical and petrophysical properties of a reservoir once CO₂ has been injected requires an understanding of how mineral dissolution and precipitation proceed. The dissolution of CO₂ in groundwater in contact with an scCO₂ plume leads to a decrease in the pH of pore fluids, driving the system far from equilibrium and accelerating the dissolution of minerals in the reservoir. Experiments exposing a siltstone to CO₂ saturated fluids have shown that the dissolution of carbonates and clays, including chlorite, lead to increased porosity and permeability in a sample of a siltstone caprock [1].

The dissolution kinetics of chlorite have been extensively studied [2], but not under CO₂ saturated conditions. Here we present the results of batch reactor experiments on a clinochlore chlorite (CCa-2, The Clay Minerals Society); testing the potential effects of pH, chloride and bicarbonate concentration, temperature and pressure (pCO₂) on the dissolution rate of the mineral. The dissolution rates observed are of a comparable magnitude (c. -12 log mol m⁻² sec⁻¹ at 50°C) to previous studies, but the proton promoted dissolution process of 19 kJ mol⁻¹ is calculated assuming a simple empirical rate law with an Arrhenius form. This result is much lower than the activation energy of 88 kJ mol⁻¹ previously reported under acidic conditions [3], and often used in geochemical models under all pH regimes. However, it is consistent with the results of a recent study using flow-through techniques [4].

The reactivity of microbially-reduced goethite: assessing the potential of a naturally-occurring waste material for mine drainage remediation

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Naturally occurring iron (Fe) oxides are ubiquitous in nature, particularly at abandoned mine sites where extraction processes have resulted in the oxidation of Fe-bearing sulphide minerals. Goethite, an Fe(III) oxide, is stable over a wide range of Eh and pH conditions and is present at several coal mine drainage treatment systems in the South Wales Coalfield, UK.

Microbial investigations at the Ynysarwed mine in the Coalfield revealed the presence of bacteria closely related to known Fe(III)-reducing species within the goethite deposit. Microcosm experiments designed to investigate the activity of these naturally-occurring bacteria were prepared using sodium acetate as the electron donor and the naturally occurring goethite as the electron acceptor.

After 100 days the solid phase Fe(II) content was determined and the results show an increase from ~1.5% Fe(II) in the starting material to ~9% in the microbially-reduced material. No increase in Fe(II) was observed in the kill or live controls. Dilute acid extractions (0.1M HCl) of the material, designed to solubilise Fe(II) weakly bound to the goethite crystal surface, recovered 97-99% of the total Fe(II).

The ability of Fe(II) bound to the surface of goethite to reduce potentially harmful elements has been shown in several studies. The reactivity of microbially-reduced natural goethite and its ability to remove problematic elements, such as zinc (Zn), from natural mine waters through addition of the slurried reduced material (5g L−1 dry weight) was investigated. The results show a 5-fold increase in Zn removal from a circumneutral mine water when compared to natural goethite. These data show the potential of naturally-occurring mine waste for the remediation of contaminated mine waters.

The Fate of Small Active Margin River POC in the Marine Environment

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Small active margin rivers export a mixture of particulate organic carbon (POC) pools derived from contemporary primary production, aged soils and uplifted sedimentary rocks. These pools are expected to exhibit a wide range of reactivities in the marine environment because of their vastly different ages and diagenetic histories. The stable carbon and radiocarbon isotopic compositions of sedimentary POC and pore water dissolved inorganic carbon (DIC) from the Waiapu River shelf, New Zealand were measured to determine the fate of the exported riverine POC. The Waiapu River exports material that is dominated by fossil C derived from the rapidly eroding Cretaceous to Paleocene mudstones (riverine POC Fmod ~0.3). Shelf sediments incorporate both riverine and marine POC as indicated by an enrichment in 13C and accumulation of 14C-rich material (Fmod ~ 1).

Porewater DIC carbon isotope compositions are controlled primarily by the addition of remineralized organic carbon to a seawater background. In the case of the Waiapu shelf, DIC δ13C values indicate preferential oxidation of terrestrial OC nearshore (~60 meters water depth) with a transition to more marine C-supported remineralization further offshore (80-130 m water depth). In all cases, the remineralized C is modern in age, thus no appreciable oxidation of fossil C or aged soil C is evident.

Oxidation of the modern terrestrial OC is far from complete based on POC isotopic data from both the Waiapu and the adjacent Waipaoa system. The terrestrial OC is well preserved in areas of fine-grained sediment accumulation as a result of rapid and episodic deposition. On balance, we argue that small active margin river continental margins have the potential to be efficient carbon sinks regardless of POC age.
Expanding potential source area studies of dust in East Antarctica by integrating trace element chemistry and radiogenic isotopes

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By studying dust records preserved in Antarctic ice cores, we can evaluate variability in dust source areas over geologic timescales. For instance, it has been determined that during the Last Glacial Maximum (LGM), South America was the dominant dust source for the entire East Antarctic Plateau [1,2], whereas ice core analyses from the Talos Dome reveal that the fraction of large particles deposited during the Holocene was significantly greater than during the LGM, indicating contribution from proximal, Antarctic sources. These findings differ from cores drilled further inland on the East Antarctic Ice Sheet (EAIS), such as the Dome C core [1,3,4].

Here we provide new results of trace Rare Earth Element (REE) chemistry and Sr-Nd, Hf signatures of <5µm diameter and bulk samples from 19 potential source areas (PSAs) in northern and southern Victoria Land (NVL and SVL), including from the ice-free McMurdo Dry Valleys (MDV). Because records from the Talos Dome currently suggest that ice-free areas such as the MDV may be important sources for local, wind-driven dust transport on the EAIS after the LGM, we expect to observe similar trends when comparing our PSA samples from SVL to Holocene dust profiles from the Taylor Dome core, and likewise from NVL to Holocene profiles in the Talos core. 87Sr/86Sr and 143Nd compositions from our PSAs are similar to existing PSA records from Antarctica.

At present, Sr and Nd isotopic systems are commonly used to identify dust provenance in Antarctic ice cores [1], however, such studies have yet to be complemented with Hf signatures and REE chemistry. Thus, forthcoming results from this study may be especially useful for distinguishing dust flux evolution during the last deglaciation.


Modelling the migration of mercury in a column experiment: biotic against abiotic mechanisms

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Apart from the behavior of mercury in terrestrial surface aquatic environment, few data are still available concerning its migration in subsurface and deep aquifers. A column experiment had been design in order to reproduce the Hg methylation by sulphate and iron reducing bacteria. Based on the experimental results, a modelling exercise had been carried out to enlighten the chain of reactions responsible for methylmercury formation in such an environment.

The numerical modelling is realised by using the PhreeQ-2 code [1] and the Thermomdem database [2]. The hydraulonics of the column is first parameterized by modeling a tracer test, allowing to realistically adjust a double porosity model. Then, the inorganic part of the model inputs include the solid substrates used (silicic sand + iron hydroxydes previously spiked with a mercury nitrate solution) and the inflowing solution. In the latter cases, this includes the chemical perturbations induced by three successive bacterial inoculation events. The organic part of the model strats from the innoculum preparation and takes into account the nature of the bacterial load (sulphate and iron reducing) and the addition of an organic substrate (Na-Lactate).

For the parameters pH, Eh, [S]T, [Fe]T and [Hg]T, a satisfactory agreement is found by considering only the inorganic part of the chemical system. The total dissolved mercury concentration is slighlty improved by adding a non electric Hg surface complexation model. Methyl mercury is also produced. However, its amount in the analysed samples is shown to depend strongly on the presence of potential methyl donors in the inflowing solution.

Computational science in nuclear waste management: ab initio investigation of f-elements bearing Monazite.

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A safe disposal of nuclear waste is of great importance not only for the nuclear engineering but also for the general safety of society. One of the challenges in nuclear waste storage is to find suitable materials that are able to immobilize minor actinides such as Np, Am and Cm. The monazite-type orthophosphates are known to be able to incorporate actinides into their structure and preserve their crystalline character. Because of its resistance to radiation damage and chemical durability monazite is a promising host matrix [1]. In our institute we perform systematic experimental and computational studies of monazite ceramics that aim into in-depth understanding of the properties of these materials and their behavior upon incorporation of actinides. In our research we extensively use first-principles calculations to complement the experimental effort. Combination of both approaches allows us to learn how to reliably compute “tricky” 4f and 5f materials using modern methods of computational quantum chemistry.

In this contribution we present a systematic first-principles studies of the structural, thermodynamic, electronic and vibrational properties of Monazite-type LnPO4 ceramics (where Ln=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy). The calculations were performed using Density Functional Theory (DFT) with different variations of the generalized gradient approximation as well as with the DFT+U approach to correct for the strong on-site Coulomb repulsion. We calculated the structural parameters, vibrational frequencies, and the enthalpies of formation as well as the excess enthalpies of solid solutions of these compounds. Our results are confronted with a variety of experimental data (structural data [2,3], solid formation and solution enthalpies [3,4], IR and Raman spectroscopies [3,5]) and previous DFT calculations [3]. We will show that such a comparison allows for a proper assessment of the computational methods, and a better constraint of Hubbard U parameter for DFT+U method.

First-principles investigation of equilibrium iron isotope fractionation in oxide and sulfide minerals

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The equilibrium isotope fractionation factor between two phases, which is a key parameter for the interpretation of isotopic variations among natural samples, can be determined from their reduced partition function ratios, also called β-factors. In most cases, β-factors cannot be measured directly but they can be calculated from vibrational properties following various approaches. For solids with Mössbauer-sensitive elements like Fe, the β-factor can be determined either from Mössbauer spectroscopy by measuring the temperature dependence of the isomer shift [1], or from nuclear resonant inelastic X-ray scattering spectra (NRIXS) by measuring the partial density of states of the resonant atom or by using the moments of the raw NRIXS spectrum [2,3]. An alternative approach consists in determining the theoretical vibrational density of states of the solid using first-principles calculations [4].

In this presentation, the Fe β-factors of oxide and sulfide minerals (mainly hematite, goethite and pyrite) computed using first-principles methods based on density functional theory with or without the addition of a Hubbard U correction (DFT and DFT+U) will be compared with the available Mössbauer- and NRIXS-derived data. While all three methods must give consistent results, discrepancies are observed in some cases. The possible sources of discrepancy will be discussed.

Cosmogenic $^3$He and $^{10}$Be production rates at high elevation (> 3800 m)

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Recent cross-calibrations of cosmogenic $^3$He in pyroxene and $^{10}$Be in quartz [1] showed that, at low elevation (< 2000 m), the $^3$He/$^{10}$Be production ratio was probably ~40% higher than the value of ~23 initially defined in the 90's. This recent update is consistent with the last independent determinations of the sea level high latitude production rates of $^{10}$Be and $^3$He, that are about 4 and 125 at.g$^{-1}$yr$^{-1}$, respectively [e.g. 2, 3]. However, major questions remain about these production rates at high elevation, notably because the elevation dependence of the $^3$He/$^{10}$Be production ratio is controversial [4]. It is thus crucial to produce new high precision cross-calibration data at high elevation.

Here we report new precise measurements of $^3$He in pyroxenes and $^{10}$Be in quartz, from dacitic moraines located at 4820 m in the Southern Altiplano (22°S, Tropical Andes). The obtained $^3$He/$^{10}$Be production ratio is 33.3±0.9 (1σ). This value is statistically indistinguishable from the production ratio measured at 1333 m [1], which reveals that the $^3$He/$^{10}$Be production ratio in pyroxene and quartz is almost invariant with elevation. When combined with the absolute $^3$He production rate locally calibrated in the Central Altiplano, at 3800 m, from a 15.3±0.5 ka old surface, these new data permit to define the absolute production rate of cosmogenic $^{10}$Be at high elevation. After scaling to sea level and high latitude, this calibration yields a sea level high latitude $P_{^{10}Be}$ ranging from 3.7±0.2 to 4.1±0.2 at.g$^{-1}$yr$^{-1}$, depending on the used scaling scheme.

This new refinement of the cosmogenic dating tool will significantly improve both the accuracy and the precision of paleoglacial chronologies in the Tropical Andes.


Calcium isotopes in evaporites constrain sulfate- vs calcite-rich seawater chemistry

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The calcium-isotope behavior of evaporite formations is proposed as a new method for constraining the composition of ancient seawater. Evaporite cycles that reach the halite facies are expected to record a different range of calcium-isotope values depending on the initial major-element chemistry of seawater. In the modern ocean, where sulfate is far in excess of calcium (28 mmol/kg SO$_{4}^{2-}$ compared to 10 mmol/kg Ca$^{2+}$), approximately 90% of the initial calcium is removed as carbonate or sulfate minerals by the time halite saturation is attained. In contrast, an excess of calcium relative to sulfate, as suggested for intervals such as the Cretaceous and the Silurian [1], leads to significant depletion of sulfate, but a much smaller proportion of calcium removed at the point of halite saturation. Isotopic fractionations associated with the precipitation of carbonates, gypsum, and anhydrite lead to Rayleigh distillation of calcium within an evaporite basin, where precipitates from more concentrated brines become enriched in the heavy isotopes of calcium, dependent on the total amount of calcium removed. The range in calcium-isotope ratios obtained by sampling different stages of the carbonate–sulfate evaporite facies is therefore diagnostic of initial sulfate- or calcium-rich seawater.

In beaker evaporation experiments, the $\delta^{44/42}$Ca value of modern sulfate-rich seawater becomes enriched by 1.2‰ from its initial composition to the beginning of halite precipitation, whereas the $\delta^{44/42}$Ca of a calcium- and sulfate-poor solution evolves by <0.2‰. The $\delta^{44/42}$Ca values of accompanying precipitates demonstrate the same characteristics, but are offset from the fluid by 0.5–0.7‰. Analyses of geological evaporites from various Phanerozoic periods show how this behavior translates to natural samples as well. This new method provides an independent test for variations in the major-element chemistry of paleoseawater.

The study of the ferriterous mineral water in Kareliya by isotopic and chemical tracers.

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From 1979 to 2012 the ferriterous mineral water in Karelia (northwest of Russia) was studied by monitoring the isotope and chemical tracers.

In 1979-1980 stable isotopes (2H, 18O) had fractionated composition (on the plot δ2H vs. δ18O the points shifted right from the meteoric line), which was caused by cryogenic metamorphism at partial freezing of water in the last glacial period. The composition of stable isotopes has strongly changed for the last 25 years (the points fit on the global meteoric line now). Other isotope tracers (13C, 3He, 4He, 20Ne, 234U/238U, 3H) also have changed and become closer to the recharge water. So the isotope data show that the water of the studied area in 1979-1980 was formed by mixing "old" and "young" components. But now we observe the rapid penetration of the atmospheric precipitation and gradually disappearance of the "old" component.

Selenium distribution linked to monsoon climate in the Chinese Loess Plateau

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Selenium (Se) is a vital trace element for human health with a narrow range between deficiency and toxicity. Diets deficient in Se have been linked with various diseases, while those with an excess can lead to toxicity. Predicting where Se deficiency/toxicity occurs is challenging due to the heterogeneous terrestrial distribution of Se and limited knowledge on what controls this heterogeneity. It has been proposed that the largest natural flux of Se to the terrestrial environment is via wet deposition from the atmosphere.

Our research uses the loess-paleosol and red clay deposits on the Chinese Loess Plateau (CLP), the largest area of windblown sediments on Earth and one of the best available records of climate change, to elucidate how atmospheric deposition of Se relates to its terrestrial distribution. We present a 6.8Ma record of variation in the Se concentration in the Lingtai section from Central CLP. In interglacial climatic periods from 2.31-1.56Ma and 1.6-1.3Ma, we find very strong positive correlations (R²=0.97 and 0.85 respectively) and we find dust input plays a greater role. As both precipitation and dust inputs are determined by the strength of the East Asian Monsoon, we are able to show that Se deposition in the CLP (at the Lingtai section), is directly related to past changes in the monsoon climate system.
Methanotrophic bacteria drive seasonal anoxia and the formation of a benthic nepheloid layer in a deep alpine lake

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We investigated the composition and formation mechanisms of a seasonal benthic nepheloid layer (BNL), a layer of high suspended particle concentration, in the monomictic southern basin of Lake Lugano. During stratified water column conditions, lasting from early summer until winter mixing in January/February, the BNL developed from the sediment-water interface and expanded 20–30 m into the water column, in tandem with the rising redox transition zone. Methanotroph-derived fatty acids (C16:1ω5-ω8), with δ13C values as low as -90‰, dominated the fatty acid pool within the BNL. Based on C-isotope data, we calculated that up to 98% of the lipid carbon is methane-derived, suggesting that the BNL is primarily composed of aerobic methane oxidising bacteria. The lipid composition indicates that the methanotrophic community in the BNL in Lake Lugano is dominated by Type I methanotrophic bacteria. Total cell numbers ranged between 0.9 and 3.6 × 10^6 cells mL^-1 during full development of the BNL. In incubation experiments we determined CH4 turnover rate coefficients that translate into potential CH4 oxidation rates as high as 20 µM d^-1. The corresponding cell-specific rates were up to 49 × 10^-5 pmol cell^-1 h^-1, which is reasonable for Type I methanotrophic bacteria. CH4 oxidation in the BNL was limited by the diffusive supply of O2 from the upper hypolimnion, implying that CH4 oxidation is the primary driver of the seasonal expansion of the anoxic bottom water volume, and explaining the vertical migration of the BNL in response to its own O2 consumption. Our study demonstrates that methanotrophic activity at the interface between oxic and anoxic water masses can drive the formation of a BNL. Such a layer of high bacterial density and high CH4 oxidation potential may thus function as an efficient CH4 barrier, preventing CH4 transport into surface waters, and eventually evasion to the atmosphere.

Niobium Mineralization in a Magnetite-Rich Carbonatite, Elk Creek, Nebraska (USA)

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The Elk Creek carbonatite is a roughly circular 7km x 7km intrusive carbonatite-alkaline syenite complex located in Southeast Nebraska. The complex is overlain by younger marine sediments and quaternary glacial till – No surface exposure exists, but drill cores collected by Molycorp in the 1970s-80s have been made available to the public for research. The carbonatite comprises several geochemically distinct intrusive phases with notable anomalous enrichment in rare earth elements and niobium. These phases include a dolomite-magnetite carbonatite (“magnetite beforsite”) phase which consists of two lobes, each approximately 0.1 square kilometer in size and extending downward to the maximum extent of drilling (900 meters). This dolomite-magnetite carbonatite is typically an aphanitic microbreccia including accessory apatite, biotite, and pyrite. Hematite dusting on mineral surfaces is pervasive, and veining is widespread. Fragments of dolomite-magnetite carbonatite are also present in a spatially-associated breccia along with fragments of apatite-dolomite carbonatite.

XRF analysis of a powdered bulk sample of the dolomite-magnetite carbonate yields data that indicate that the dolomite-magnetite carbonate differs from other carbonatite phases in that it has much higher Ti, Th, and W compared to the other intrusive phases. It also differs from the other intrusive phases in that Fe > Mg and it is depleted in light REE relative to the other rocks. The magnetite carbonate also contains micron-scale (0.01-0.10mm diameter) accessory niobium pyrochlore, disseminated in dolomite and biotite, in economically-significant concentrations (10.000ppm or higher Nb in bulk sample). The prevalence of pyrochlore across the entire complex is directly related to the presence of this dolomite-magnetite carbonatite.
Tuning the Torch for Lead Isotopes: The Battle in Lugdunum

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To celebrate Francis Albarède’s pioneering work in developing high-precision, high-throughput Pb isotope analysis by Tl doping and sample-standard bracketing MC-ICP-MS [1], I here review some selected contributions by the Lyon group to cosmochemistry, geochronology, Mars, mantle geochemistry, and archeometry using this technique. The superior precision of MC-ICP-MS compared to unspiked Pb TIMS work led us to revisit several classic but crucial questions involving Pb isotopes. We determined the age of the Solar System from Pb-Pb measurements of refractory inclusions in meteorites [2], a result only now confirmed by independent means despite tumultuous revisions of U isotope compositions and major improvements in analytical precision and blanks since our early work. We further re-determined the initial Pb isotope composition of the Solar System and the solar nebula Th/U [3] and found Pb isotope evidence that some asteroids accreted and differentiated within only one million year of the formation of the Solar System [4], thereby placing constraints on nebular evolution. Our Pb-Pb ages of SNCs [5], the shergottites in particular, are important because they finally bring the ages of Martian meteorites (4.1 Ga) into agreement with cratering chronology and satellite observations for Mars, as well as with extinct radioactivities, but are controversial because ages inferred from other chronometers are far younger (160 Ma). The high throughput of MC-ICP-MS further changed the geochemical approach to understanding mantle heterogeneities in volcanic time series, such as in Hawaii [6], and the exploring of length and time scales of isotopic heterogeneities along the world’s mid-ocean ridges and, hence, the deep Earth, allowing for full-fledged spectra amenable to physical and statistical modeling to be obtained [7, 8]. A spectacular new result is the evidence of Pb-Hf isotopic ‘toggles’ along the SEIR, and their random distribution, indicating that the local mantle has lost all memory of its mixing history [9]. Another key result was the Pb-Hf correlation in Hawaiian lavas showing that entrainment of the upper mantle by plumes is minimal [10]. We currently apply Pb isotopes to tracking Pb ore provenance in ancient Rome in order to shed new light on the heavy metal record of local economic activity, urban development, and warfare.

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Impact of long-term nitrogen deposition on the fate of nitrogen in peatlands

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Large areas of northern peatlands in Europe and North America have been affected by elevated long-term nitrogen deposition at levels of 0.5 – 2 g N m⁻² yr⁻¹, and in extreme cases up to 5 g N m⁻² yr⁻¹. The consequences of this deposition for the fate of nitrogen, especially the allocation of the element between vegetation and peat and the mobility in dissolved form, and for the carbon cycle are only poorly known to date. We investigated this issue using ecosystem modelling based on a long-term fertilized site and experimentally with mesocosms from five different European peatlands that have been exposed to range of 0.2 to 5 g N m⁻² yr⁻¹. The mesocosms were placed in a greenhouse under controlled light and water table conditions for a period of 160 days after an initial equilibration period. We added a¹⁵N-NO₃ tracer with irrigation water to determine how the allocation of nitrogen in these peatlands differed and also investigated the carbon exchange and productivity of the sites under these conditions. The results show that the Sphagnum moss layer was not severely impaired at any site and that even under severely N polluted conditions nitrogen was still taken up by the moss layer. The effectiveness of the moss filter for the element declined, however, and some breakthrough occurred, whereas nitrogen in the pristine sites seemed to be indirectly transferred into peat by the root system of vascular plants. Overall more nitrogen was taken up by vascular plants in the more polluted sites. Elevated nitrogen deposition lead to raised ammonium and DON concentrations even at lower deposition levels but strongly elevated nitrate concentrations only occurred at the most polluted site. Substantial differences in carbon cycling between sites did not occur in the mesocosms experiments. The ecosystem modelling exercise using the new model PEATBOG showed that the most important impacts of nitrogen deposition are to be expected are through indirect changes in the ecosystem structure, which was altered from moss to shrub and then grass dominated in the simulated system. The replacement of plant functional types lead to a higher rate of nitrogen processing in the system and higher productivity and carbon uptake. Also in the simulations the peatland remained a sink of nitrogen with only moderately raised nitrogen export.

Characterization of metabolically active microorganisms in an hydrothermal active field in the Okinawa Trough (IODP Exp. 331)

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The BGR project, as part of the post-cruise research of IODP Expedition 331, Deep Hot Biosphere, shall test the hypothesis that the quantitative microbial community composition and the cultivable microorganisms in hydrothermally influenced deeply-buried marine sediments are significantly different from those in cold and temperate deeply-buried marine sediments. The previously successfully applied molecular techniques real-time PCR (qPCR) and catalyzed reporter deposition - fluorescence in situ hybridisation (CARD - FISH) shall be used as well as cultivation and stable isotope-probing to proof the existence of a deep hot biosphere, to describe it and to isolate novel microorganisms. The domains Archaea, Bacteria and Eukarya as well as the JS1 candidate group, Chloroflexi, Geobacteraceae, Crenarchaeota and the functional genes dsrA, mcrA, aprA, and Rubisco (cbbL) have been quantified via qPCR. All genes have been detected in different copy numbers. The overall order of abundance is Archaea > Bacteria > Eukarya. Directly after IODP Expedition 331 in October 2010, culture media were inoculated with IODP samples at different temperatures and the enrichment cultures are maintained since then. Growth is continuously checked about every three months and in case of growth, colonies are picked and transferred to fresh media. Several aerobic and anaerobic enrichments have been obtained so far. To explore microbial activity in the original samples microcalorimetric measurements showed a considerable activity at 90°C which was partly attributed to microbial activity. The microcalorimetric measurements revealed activity of thermophilic microorganisms in the IODP Exp. 331 samples.

Sulfur and iron speciation in warm deep sediments affected by dry deposition of iron

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The Gulf of Aqaba is a unique natural laboratory for a research of the impact of atmospheric dry deposition on biogeochemistry of marine sediments. Atmospheric iron deposition is 3.65 mmol m⁻² year⁻¹ [1], and total iron content of sediment at 700 m depth is 2.0 – 5.7 mmol kg⁻¹ wet sediment. We sampled sediment at four locations with various overlying water depths.

At water depths 300 – 700 m the depth of oxygen penetration into warm upper sediment (c.a. 21°C) is 8-14 mm. In anoxic sediments, combination of moderate TOC content (0.1-0.6%) with high sulfate concentration (32 mM) fuels organoclastic bacterial sulfate reduction. Concentrations of Fe(II) in the pore-waters are as high as 78 µM, and concentrations of dissolved Mn are as high as 76 µM. Combination of low hydrogen sulfide concentration in pore-waters (<0.37 µM), low concentrations of soluble sulfide oxidation intermediates ([S²O₃⁻²] < 0.55 µM, [SO₃⁻²] < 0.14 µM) and low sedimentary S₀ content (≤0.37 mmol kg⁻¹ wet sediment) indicate that transformation of hydrogen sulfide to pyrite is fast enough to prevent sulfide oxidation by Fe(III) phases. Pyrite is the main sulfur pool in the sediment solid phase, and its content is up to 10.6 mmol kg⁻¹, with a maximum at 15 – 25 cm b.s.f.

At the shallow sediments (21 m water depths) penetration depth of oxygen is only 1 mm, and hydrogen sulfide concentration in pore-waters is as high as 12 µM. Dissolved iron and manganese concentrations below 5 cm b.s.f are lower than in the deeper sediments <1 µM and <0.5 µM, respectively. Concentrations of sulfide oxidation intermediates in pore waters ([S₂O₃⁻²] < 4.05 µM, [SO₃⁻²] < 3.64 µM) as well as in the solid phase [S₀] = 0.07-1.37 µmol kg⁻¹ wet sediment are higher than at deeper locations.

The sediment of the Gulf of Aqaba presents an interesting example of transition of pore-water composition with depth from sulfidic (H₂S-rich) to ferruginous (Fe(II)-rich).


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Mass independent isotope fractionation of mercury: Why it is such a useful tool in biogeochemistry and ecology

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Mercury is a globally distributed and highly toxic heavy metal with both natural and anthropogenic sources. Its mobility, toxicity and bio-accumulative properties change dramatically as it is transformed through microbial, photochemical and dark abiotic reactions in the environment. Multiple biogeochemical transformations of mercury determine its movement and bioavailability, and knowledge of these processes can aid in developing strategies for minimizing human and wildlife exposure to its most toxic forms. The seven stable isotopes of mercury fractionate in the environment due to an unusually wide range of physical processes. Mass-dependent fractionation (MDF) occurs during most biotic and abiotic reactions that have been investigated. Mass-independent fractionation (MIF) of mercury can be caused by the magnetic isotope effect, the nuclear volume effect and by UV self-shielding. Each fractionation mechanism imparts a diagnostic pattern of isotopic variation and thus mercury isotope ratios can be used to unravel complex biogeochemical pathways for mercury. Large-magnitude MIF of odd isotopes is uniquely produced by photochemical reactions, which are important because they can degrade mercury from the toxic methylated form to a volatile gas. In addition to isotopic fingerprinting of sources, MIF and MDF in natural samples have been calibrated against experimental determinations of fractionation factors to identify reactions in natural systems and estimate their reaction progress. Because MIF is unaffected by biotic processes it preserves a memory of biogeochemistry before entry into the base of foodwebs.

Seawater Trace Metals in acidified condition: an accumulation study in the blue mussel Mytilus galloprovincialis off Vulcano Island submarine vents (Italy)

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Ocean acidification is linked to the increasing concentration of atmospheric anthropogenic carbon dioxide, and this process might have negative ecological and economic effect worldwide.

Areas with naturally high levels of CO2 can help us to achieve a better understanding of this issue. Submarine vents in the Levante Bay of Vulcano Island (Italy) are CO2-dominated resulting in seawater acidification, and producing a stable pH gradient (from 8.2 down to 5.5) across the bay [1].

We now know that ocean acidification is tightly linked to the mobility and bio-availability of heavy metals.

In that area a transect covering the pH conditions which will be found up to the end of this century has been individuated and a Blue Mussels transplant experiment was done along this gradient in order to estimate the trace metal accumulation capability related to the seawater acidification.

Major and Trace elements were analyzed both in seawater and in the mussels’ tissue.

At the end of the experiment, the animals showed an increase of concentration for some elements such as Fe and V with respect to blanks.

The present study provides preliminary data on a particular aspect related to the ocean acidification problem.

MgSO₄ phases: hydration, spectroscopy and S isotope partitioning

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We study the relative stability of several magnesium sulfate minerals using first-principles calculations based on the density functional theory in the ABINIT implementation. These phases might be present on the surface of Mars or on a variety of smaller icy bodies form the outer solar system. Our calculations show that, if involved in the water cycle of Mars, the magnesium sulfates must be already present as hydrated phases: the anhydrous phases are easily absorbing water and, in turn, the complete dehydration of these phases requires large temperature, unattainable on Mars. We equally compute the Raman and infrared spectra of several phases to offer reference spectra for in situ spectroscopic identification. Apart from the appearance of the water bands, the hydration also changes the position of several lower-frequency bands. Using the spectroscopic calculations we determine the influence of hydration on the S isotope partitioning. We show that it is highly dependent on the temperature. For temperatures specific to the surface of Mars, hydration of the anhydrous phase leads to an enrichment in the S³⁴. The effect on the already hydrated phase is opposite: further hydration enriches lighter isotopes.

Partitioning of trace elements between Na-bearing majoritic garnet and melt at 8.5 GPa and 1500–1900°C

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The new experimental data on trace element partitioning between Na-bearing majoritic garnet and melt at 8.5 GPa and 1500–1900°C applicable to partial melting of Na-rich eclogite is presented. The Na-bearing garnet is a liquidus phase of the system at 1850–1650°C being accompanied by enstatite-rich pyroxene at lower temperatures. With the temperature decrease, Na concentration in garnet increases up to >1 wt % Na₂O due to progressive incorporation of Na majorite (Na₂MgSi₅O₁₂). Most of the studied trace elements are incompatible, except for Er, Tm, Yb (in some runs), Lu, and Sc (in all runs), which partition into garnet. The main feature of the trace-element partitioning in our experiments is the different behaviour of the LREE (La, Ce, Pr) in comparison with MREE and HREE (Nd, Sm, Eu, Tb, Dy, Y, Ho, Er, Tm, Yb, and Lu). Significant increase of D values for LREE with increase of Na₂O concentration in garnet is observed. As predicted from lattice strain, partitioning coefficients for REEs entering the X site of garnet exhibit a near-parabolic dependence on ionic radius. Other elements including the LILE (Rb, Sr, Ba), Sc, as well as Zn, Ta, and Pb have a clear affinity for aluminosilicate melt. The results of the study are applied to the formation of inclusions of Na-bearing majoritic garnets in diamonds and equilibrium melts, which are significantly enriched in LREEs being very similar to kimberlitic and OIB melts.

This study was supported by the Russian Foundation for Basic Research (project no. 12-05-00426).

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Nitrifying potential in *Beggiatoa* mats from marine mangroves

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Marine mangroves are intertidal marine ecosystems found in tropical and sub-tropical areas. A development of white bacterial mat can be found in Guadelouian marine mangroves. This mat consists of a layer of micro-organisms deposited above the anoxic sediment consisting of eukaryotes (e.g. diatoms, nematodes) and prokaryotes (e.g. filamentous cyanobacteria, filamentous sulfur-oxidizing bacteria, archaea). Most of the filamentous bacteria found in the mat belong to the genus *Beggiatoa*. These bacteria contain genes encoding both for sulfur oxidation (production of sulfate) and ammonium oxidation (production of nitrate).

The aim of this study was to determine the potential for nitrification in these *Beggiatoa* mats. Potential nitrification rates were carried out with the *Beggiatoa* mat collected in a marine mangrove. The *Beggiatoa* mat or filaments were amended with sea water containing different NH4+ concentrations and incubated under oxic conditions. The increase in nitrate concentration was measured after 15 hours of incubations. Potential nitrification rates showed a large variation ranging from 0.2 to 2200 µg nitrate N L⁻¹ h⁻¹. Our study showed the potential for nitrification in *Beggiatoa* filaments, implying an important link between the N and S cycles, by sulfur oxidizing bacteria, in these mangrove systems.

Examination of Magma Degassing Paths Based on Melt Inclusions

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In a landmark paper, Newman *et al.* [1] suggested that the CO2 and H2O contents of volcanic glasses could be used to understand magma degassing processes. This approach was immediately adopted by Anderson *et al.* [2] and applied to melt inclusions (MI) in quartz phenocrysts from the Bishop Tuff to investigate the pre-eruptive volatile contents and pressures in the magma chamber during phenocryst growth and MI entrapment. In the nearly three decades since these pioneering studies, numerous MI studies have been conducted to determine magma degassing paths using this method.

The scientific basis for using CO2/H2O systematics in MI is robust and supported by experimental data, but several unstated assumptions are required for the results to accurately define a magma degassing path. First, the trapped melt must have been at volatile saturation. Additionally, the melt (glass) that is analyzed must represent the melt that was originally trapped and must be free of any post-entrapment modifications (or it must be possible to reverse these processes before analysis or account for these changes by other means). Thus, post-entrapment crystallization on the walls of the MI, diffusional loss of H2O from the MI and exsolution of a vapor bubble after MI entrapment are all processes that will affect the CO2/H2O systematics of the MI.

Examination of data from a variety of sources suggests that in many cases there is clear evidence for post-entrapment modifications (primarily shrinkage bubble formation) that have not been corrected for during analysis or data interpretation. Moreover, recent studies have shown that these modifications can produce “false degassing paths” that cannot be distinguished from true degassing paths. It is also critical that MI be studied within a paragenetic context in order to constrain relative times of MI formation, and that other indicators of crystallization progress and/or depth of formation be monitored along with the CO2/H2O systematics to confirm that the volatile data record a degassing history.

The Torres del Paine (~12.59 Ma) intrusion consists of three granite and four mafic batches, which formed within 160 ± 11 ka (Michel et al. 2008, Leuthold et al. 2012). It intruded into fine grained pelites, sandstones, and conglomerates of the Cerro Toro and Punta Barrosa formations at a depth of 2-3 km. Its contact aureole is characterized by the occurrence of porphyroblastic cordierites (crd). The crd forming reactions are the chlorite break-down reaction (ca. 480°C) and the phengite break-down reaction (530-550°C), which is accompanied by a modal decrease in biotite and the appearance of k-feldspar.

We present differences of crystal size distributions (CSDs) in a 400m long sample profile from the igneous contact to the outer part of the aureole. Samples close to the contact have the smallest crystals (radius < 0.06mm), while samples at 400m from the intrusion contain the largest crystals (radius < 0.09 mm). The maximum population density decreases from the outermost contact aureole to 9.5mm^-4 at 400m from the intrusion to 11.5mm^-4 close to the intrusion. The resulting parameters indicate rapid completion of nucleation before the thermal peak in the inner parts of the contact aureole, and continued reaction after the thermal peak in the outermost contact aureole. In the innermost part of the aureole the overstepping is several tens of degrees (50-150 °C), depending on the nucleation model and the choice of parameters. Calculations with these parameters further show a narrow transition zone (~5m width) of full reaction to no reaction between the prograde contact aureole and the unreacted host rock, indicating a relatively sharp isograd for sampling purposes.

Interpretation of Calcium Isotope Variations in Marine Fossil Records

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Many studies indicate the existence of calcium isotope excursions and trends in sequences of fossil marine carbonates (e.g.[1, 2]). However, interpretation of these calcium isotope variations is still controversial [3]. Several studies explain calcium isotope excursions as indicators of an imbalance between the major calcium fluxes in the oceans, riverine input and output by carbonate sediments (e.g. [2, 4]). These studies tend to neglect the direct coupling between calcium and carbonate ion fluxes in both weathering and carbonate precipitation. As a consequence the neglect may lead to very unlikely scenarios for the corresponding ocean carbon cycle. Here we present a simple numerical model to calculate mass balances for both marine calcium and carbonate ion concentrations in response to changes in the weathering and carbonate sediment fluxes. The model results clearly show that neither weathering nor carbonate sedimentation may explain observed calcium isotope variations unless extreme scenarios for the inorganic carbon cycle are assumed. Hence alternative explanations other than weathering and carbonate sedimentation are necessary to explain the calcium isotope excursions observed in the Phanerozoic record.

Yet for interpretation of the marine Ca isotope record it has not been taken into account that precipitation rate has a significant influence on calcium isotopes in calcium carbonate minerals [5, 6, 7]. Nielsen et al. [8] recently suggested that the influence of the Ca\(^{44}\)-CO\(_3\)\(^{2-}\) ratio on precipitation rate has a significant impact on calcium isotope fractionation. Variations of the marine Ca\(^{44}\)-CO\(_3\)\(^{2-}\) ratio by up to one order of magnitude may have occurred in the Phanerozoic oceans and may explain at least some of the observed calcium isotope trends.

Weathering processes and supergene formation of uranium bearing minerals at U-mines in the Saint-Sylvestre Area (French Massif Central)

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In France, uranium mines were exploited between 1945 and 2001 leading to the production of 76,000t of U but also 200 Mt of waste rocks. We present the supergene evolution of waste rock piles generated during mining operations at the Vieilles Sagnes site (Fanay) located in the Saint-Sylvestre leucogranite complex (northwestern Limousin, French Massif Central). This two-mica granite was emplaced at 324 ± 4 Ma and hosts an important U-ore mineralization deposited at 270 - 280 Ma, due to sustained hydrothermal circulation.

At the Vieilles Sagnes site mining operations between 1957 and 1965 generated waste rock piles of dominantly granitic rocks that have been exposed to supergene processes since the mining time. The U content of the blocks in the waste rock pile is 10-120 ppm, while in the ore body it is around 1000-3000 ppm.

To assess their supergene evolution and the neo-formation of uranium bearing phases two trenches were excavated through the waste rock pile, enabling the sampling of both superficial blocks and samples from the interior of the pile. Granitic blocks, proto-soils and alteration products that form the matrix of the waste rock pile, as well as paleo-soils underlying the rock pile were sampled.

The micromorphology, mineralogy and geochemistry of the samples representative of the different horizons of the profile investigated were examined by optical microscopy, and SEM observations, XRD and ICPMS whole rock analyses, respectively.

The degree of weathering of the granitic blocks is evidenced by the occurrence of chlorite and kaolinite alteromorphs after biotite and smectite and kaolinite after feldspar. The liberation of Fe gives rise to the local formation of Fe-phosphates and sulphates. Magmatic and hydrothermal U-bearing minerals release U as alteration and arenisation of the granites take place. So far no coffinite or uraninite from the initial mineralization have been observed.

Preliminary results suggest that the migration of uranium and formation of uranyl phosphates is at least partly associated with the supergene formation of Fe-phosphates. U-sorption onto clay minerals also seems to play an important role in decreasing U-mobility during meteoritic weathering.

Non-mass-dependent oxygen isotope enrichments in O3 and CO2: New insights from experiments, observations, and modeling

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Results from recent laboratory experiments, atmospheric observations, and photochemical kinetics modeling provide new insights into the anomalous 17O and 16O enrichments in ozone and their transfer to carbon dioxide. In particular, new observations of the triple oxygen isotope composition of stratospheric CO2 reveal surprisingly large anomalous enrichments that vary with latitude, altitude, and season. The triple isotope slopes were 1.95±0.05 (1σ) in the middle stratosphere and 2.22±0.07 in the Arctic vortex versus 1.71±0.03 from previous observations and a factor of 4 times larger than the mass-dependent value of 0.52. Kinetics modeling of laboratory measurements of CO2-ozone isotope exchange demonstrates that non-mass-dependent isotope effects in ozone formation alone quantitatively account for the 17O anomaly of CO2 in the laboratory, resolving long-standing discrepancies between models and laboratory measurements. Model sensitivities then provide a framework for understanding 17O in stratospheric CO2 and the larger three isotope slopes observed there than in laboratory experiments and, thus, a firmer foundation for the many biogeochemical and paleoclimate applications of 17O anomalies in tropospheric CO2, O2, minerals, sulfates, and fossil bones and teeth, all of which derive from isotope exchange between ozone and stratospheric CO2. Finally, measurements of the pressure and bath gas dependence of the 17O and 16O enrichments in ozone in bulk photochemistry experiments in the laboratory [1] provide new insight into and constraints on the physical chemical origin of the dynamically-driven symmetry isotope effects in ozone formation.

Algal mats of the North Pole: How sea ice melt can cause anoxic spots on the Arctic deep-sea floor

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The centric diatom Melosira arctica forms kelp-like accumulations under the Arctic sea ice, in the form of meter-long filaments, anchoring in troughs and depressions under ice floes. These mat-forming algae are extremely sensitive to warming and melting of the ice, leading to their rapid sedimentation. The research icebreaker POLARSTERN visited the ice-covered eastern-central basins between 82° to 89°N and 30° to 130°E in summer 2012 in the framework of the expedition ICEARC. By September, the Arctic sea ice had declined to a record minimum of 3.6 million square kilometers. Consequently, we observed the massive sedimentation of sub-ice algal biomass of up to 150 g C per m² to the deep-sea floor of the Arctic basins. Patches of algal mats of 1-50 cm in diameter covered up to 10% of the seafloor at 3300-4500 m water depth. in situ and ex situ microprofiling of diffusive oxygen fluxes into sediments covered by algal aggregates showed elevated rates of 5-6 O₂ mmol m⁻² d⁻¹, compared to <0.4 mmol m⁻² d⁻¹ in the surrounding sediments. Apparently only sediment bacteria, and large mobile megafauna were able to profit of the ice-algae deposition event. In cores covered by Melosira strands, oxygen penetration in the sediment was reduced to a few mm as compared to the surrounding sediment, where oxygen penetrated >50 cm deep. From the in situ oxygen profiles we conclude that the sinking Melosira strands had contributed >85% of total carbon flux to the deep-sea floor in 2012, but that such massive algal falls were previously rare. Our observations support the hypothesis that the thinning ice cover enhances under-ice productivity and export. If this phenomenon repeats seasonally, substantial changes in the biogeochemistry and biodiversity of the ice-covered Arctic basins are expected.

Figure1: Sea cucumbers feeding on freshly deposited algal mats at 4500 m water depth

Aqueous Li⁺ speciation and ancient climate monitoring

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Lithium is recognized as a valuable trace metal in the area of ancient climate monitoring. This arises from the isotopic composition of Li in seawater being strongly influenced by continental weathering, one of the major sources of Li in seawater, and the incorporation of aqueous Li⁺ into calcium carbonate shells. By systematically analyzing the isotopic composition of Lithium in ancient calcium carbonate it is possible to reconstruct a record of Li isotope fractionation (IF) in seawater over the past 68 Ma. Due to the close association of Li IF with ancient weathering, this record is able to provide critical information concerning the ancient earth climate.

Previous studies base their paleo-reconstructions on the close correspondence between modern values of Li isotope ratios in calcium carbonates and seawater. Implicit is the assumption that Li IF is not sensitive to environmental conditions such as Temperature and pH. This assumption is not supported from a molecular structure point of view; there is little information concerning the identity and molecular structure of aqueous Li⁺ species and it is not clear to what extent ligand coordination effects may play in the incorporation of Li⁺ into calcium carbonate.

We have carried out a theoretical (Density Functional theory) study of aqueous Li⁺ speciation including effects of ligand coordination, temperature and solute pH. We have calculated the isotope exchange equilibrium constant associated with the Li Acid/Base equilibrium and can constrain it to positive values. The consequences of this species dependent IF are then studied using a model for Li-Carbonate coordination. We define an effective IF to model temperature dependent IF are then studied using a model for Li-Carbonate equilibrium and can constrain it to positive values. The consequences of this species dependent IF are then studied using a model for Li-Carbonate coordination. We define an effective IF to model temperature and pH induced changes in Li IF in Li-Carbonates. We predict that under normal oceanic conditions Li IF is not sensitive to pH but may be significantly influenced by temperature.

Based on our results we revisit the basic assumption that Li IF is not sensitive to environmental conditions such as Temperature and pH. Namely, our observation of significant species dependent Li IF strongly suggests that the mechanism through which Li is incorporated into calcium carbonate is not sensitive to the Li speciation.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Geochemical spectra as an integral characteristic of the concentration and dispersion of elements in soils, peats and natural waters

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Geochemical spectra are the useful tool for comparison of elements concentration or dispersion in the different components of the biosphere. In this work elements distribution patterns were studied in soil samples from Yakutia, West Siberia and European Russia. Geochemical spectra were also obtained for particle-size fractions and ortsteins isolated from some soils of taiga zone, as well as for natural waters.

Geochemical spectra depend largely on soil mineralogical composition. Investigation of the elemental composition of sand, silt and clay fractions showed clear divergence of their geochemical spectra. Geochemical spectra of iron -manganese nodules from different horizons of sod- podzolic soils were quite similar. This suggests that they were formed in single geochemical space from similar soil formation products and in presence of similar soil solutions. This supposition also seems to be true for mineral horizons of alluvial soils and underlying peats.

This work was supported by RFBR grant No 13-0500542.


Zircon from Mesozoarchean enderbites of Volgo-Uralia: U-Pb age, REE, Hf- and O-isotope compositions

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As shown by numerous drillings, Archean charnockitic rocks are common in most of the lower crust in southern Volgo-Uralia, which is one of the major crustal megablocks of the East European Craton [1]. They are mainly enderbites that form large bodies (e.g. the Kolyvan intrusin, this study). Zircon from the enderbites contains relics of inherited cores with magmatic oscillatory zoning. These are surrounded by CL black-and-bright alternating bands of curved metamorphic rims. The crystallization age of the cores is between 3140±7 Ma (SHRIMP) and 3127±46 Ma (LA-ICPMS), while the outmost CL-bright rims are ca. 1945 Ma. The ages in-between are interpreted as a result of different degrees of Pb-loss caused by the high grade metamorphism. The ingressive recrystallization of primary magmatic zircon correlates with depletion in REE, which is observed consistently in each studied core-rim pair. No differences in O-isotope composition are detected between the cores and rims; the δ18O values vary from ca. 5 to 6.5. The Hf-isotope compositions of magmatic cores (-3 to -9 ‰ Hf) and metamorphic rims (-14 to -28 ‰ Hf), and their similar crustal model ages from 3.42 to 3.86 Ga, imply Eo- to Paleoarchean crustal sources for the charnockitic magmas and very little, if any, juvenile additions during the metamorphic event at ca. 1945 Ma. The dated Kolyvan enderbites belong to calc-alkaline, meta- to peraluminous, mainly ferroan series, also indicating substantial participation of crust in charnockitic melt sources relevant to a continental arc setting at 3.1 Ga. We reported similar results on rocks from the Bakaly block to the northeast of the Kolyvan region [1] confirming widespread Early Archean crust in Volgo-Uralia.

Element accumulation in peat of the Vidrino highmoor

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Almost 90 years ago, V.I. Vernadsky [1] created the holistic doctrine of the Biosphere where he demonstrated the primacy of life as a geological force. Concentrative function of living matter plays a significant role in biomineralization, which is the process when living organisms assemble structures from naturally occurring inorganic compounds [2].

The purpose of this work was to investigate biomineral formation in peat and show an important role of living matter in element accumulation. The objects were peat of the Vidrino highmoor (south-east of the Baikal region, Russia).

The high concentrations of Zn and Cu (500-600 g/t) were determined in peat of the Vidrino highmoor in the layers of early Holocene (390-440 cm) which were formed in period 11-8.5BP. It was shown that authigenic sulfides of Zn and Cu with micron dimension (0.5-3 μm) were formed in the plant cells of sphagnum. Also particles of native silver (5 -7 μm) were found out in the peat of the Vidrino highmoor and which were accumulated in cell membrane of sphagnum. The mechanism of silver micro-particles formation in the cell membrane of sphagnum was proposed in this work.

The obtained results show a considerable role of biogenic mineral formation in the investigated peat that is a very important result in discussion about genesis of ore formation in which the preference is given to physical and chemical processes and often the role of living matter is not considered. This research was supported by the RFBR grant 11-05-12038-ofi-m-2011 and grand OPTEC.


A tool for exploring the impact of crustal contamination: The Magma Chamber Simulator

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The Magma Chamber Simulator is a new computational tool that quantifies the impact of simultaneous recharge, assimilation and crystallization on melt±solids±fluid in a magma-recharge magma-wallrock composite system. Enthalpy from magma cooling/crystallization and recharge heats wallrock (WR). When the fraction of anatectic melt attains or exceeds a critical percolation limit of ~0.05-0.15, assimilation begins. Magma cooling/crystallization, addition of recharge magma and anatectic melt, and WR heating continue until magma and WR reach thermal equilibrium. For each simulation step, thermodynamic and material balance assessment provides major/trace element and isotopic compositions, masses and temperatures of all phases in each part of the composite system. Initialization includes bulk composition, temperature and pressure of all subsystems, as well as relevant solid/melt and solid/fluid partition coefficients. Simulation of high alumina basalt intruding doric to granitic WR at 500-550°C and 0.1 GPa yields a large volume of dacitic melt at equilibrium temperatures of 950-975°C. Assimilation enhances pyroxene crystallization but suppresses plagioclase; this and addition of anatectic melt yield a melt body up to 5x larger than that generated by FC alone. Selected trace element and isotopic results for magma show that, at the equilibrium temperature, Sr isotopes are >0.708, with only 2% of Sr contributed by crust. Nd isotopes are >0.5126, with ≤11% of Nd from crust. In contrast, the total mass of anatectic melt assimilated is ~40%, highlighting the critical difference between mass of element and total mass of assimilated melt. Trace element results also illustrate that variations in mass of element and mass of magma melt can yield dilutions of incompatible element concentrations in contaminated magma, providing an explanation for systems that have “decoupled” trace element and isotopic signatures. Because the MCS predicts detailed phase abundance, mass and compositional information, exploration of a wide range of open-system problems in igneous petrology is possible.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Mineral Surface Hydroxyl Group Identity and Reactivity

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Mineral surfaces are reactive transformation centres and sinks for gases, solutes and solvents. These surfaces are populated by (hydr)oxo functional groups that can undergo protonation, ligand exchange, and form extensive networks of hydrogen bonds (Figure 1). Knowledge of the types, distributions and orientations of these groups is consequently essential understanding molecular-scale processes taking place at mineral surfaces.

This work is focused on the properties of hydroxo groups on important crystallographic planes of synthetic nano-sized (α, β, γ)-FeOOH particles exposed to vacuum, water vapor and carbon dioxide. Vibration spectroscopic signatures of isolate and hydrogen bonded hydroxo groups on these minerals will be presented alongside predictions from molecular dynamics simulations. This body of work forms the basis for a molecular-scale understanding of reactions taking place at surfaces of geochemically relevant mineral particles.

Figure 1. Schematic representation of dominant configurations of gaseous water molecules (blue) adsorbed on the (010) (left) and the (001) (right) planes of γ-FeOOH.


Reaction chain modeling of denitrification reactions during a push–pull test

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Field quantitative estimation of reaction kinetics is required to predict biogeochemical reactions in aquifers. We extended the analytical solution developed by Haggerty et al. [1] to model an entire 1st order reaction chain and estimate the kinetic parameters for each reaction step. We then evaluated the ability of this solution to model experimental results from a push pull test in a fractured crystalline aquifer (Ploemeur, Brittany). Nitrates were used as the reactive tracer, since denitrification is a sequential reduction of nitrates to nitrogen gas occurring in a chain reaction (NO3- → NO2- → NO → N2O → N2) under anaerobic conditions. The kinetics of nitrate consumption and by-products formation (NO2- and N2O) during autotrophic denitrification were quantified by using a reactive tracer (NO3-) and a non-reactive tracer (Br-). Comparison of the Br and NO3- breakthrough curves showed that 10 % of the injected NO3- molar mass was transformed during the 12 hour experiment. Similar results, but with slower kinetics, were obtained from laboratory experiments in reactors. The good agreement between the model and the field data shows that the complete denitrification process can be efficiently modeled as a sequence of first order reactions. The variability of biogeochemical reactivity in the field will be also discussed.

Copper contamination of lake sediments in the vicinity of Konin (Poland)

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Copper is an element essential to the life of many organisms. However, excessive concentrations of copper can be toxic. Due to the harmful effects of copper to aquatic organisms, its PEC level in sediments has been fixed at 149 mg kg⁻¹.

Sediment samples were collected from the 5-cm thick surface layer of the profundal zone of 14 lakes located in the near Konin (central Poland). Determinations of the concentrations of Al, Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, Sr, Ti, V and Zn were determined by ICP-AES methods from solutions obtained after digestion in aqua regia. The Hg concentration determinations were made using TMA method and the organic carbon content (TOC) was determined by coulometric titration method.

The concentrations of the some trace elements varied over a wide ranges of content: for Cu - 9-674 mg/kg, Ba 57-409 mg/kg, Hg – 0.058-0.366 mg/kg, Ni - 5-25 mg/kg, Pb - 16-53 mg/kg, Sr - 53–758 mg/kg and Zn - 30-184 mg/kg. It has been found that the sediments of five lakes (Gosławskie, Mikorzyńskie, and Wąsosko-Lesieńskie, Płtnowskie, and Wąsosko-Mikołajewskie), whose waters are included in the power plant cooling system, are characterized by much higher content of Cu, Ba, Hg, Mn, Sr and Zn, as compared to the other lakes. The average concentrations of Cu, Ni, Pb, Hg and Zn in the sediments of the latter lakes are comparable with the sediments of five lakes. Therefore, it is necessary to perform further tests to determine the copper content in fish tissues due to the fact that these lakes are used for recreational and angling purposes on a large scale.

A comparison of Pitzer databases for nuclear waste disposal modelling

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For the modelling of different chemical aspects of a nuclear waste repository in salt rock, the Pitzer formalism is necessary. Therefore, a comprehensive database with the relevant species reaction constants and associated ion-ion interaction parameters including temperature-dependencies is required. A number of different tailored Pitzer databases are available [1]. To judge their capabilities and limitations we performed comparative calculations for well-defined chemical systems (binary or ternary solubility diagrams). To avoid possible deviations due to different speciation codes all databases where transformed into the format specific for Geochemist’s Workbench [2]. Additionally, model results are compared to experimental values from the literature.

Most results for the Oceanic Salt Systems (Na⁺, K⁺, Ca²⁺, Mg²⁺ / Cl⁻, SO₄²⁻ – H₂O) at 25 °C show a good agreement between experiment and model. At higher temperatures, sparse temperature-dependent data causes strong differences in the results.

For the radionuclides (e.g. Nd, Np), the solubility of their amorphous hydroxides in high salinar solutions was calculated as a function of pH. Missing anionic hydroxo-complex species or less reliable data produce inadequate predictions of the increasing solubility of mineral phases (e.g. fresh amorphous Nd(OH)₃ or NpO₂OH) in the strongly alkaline medium. This demonstrates the importance of complete chemical speciation data.

Caesium was chosen as example for a fission product. Only minor differences can be found in the calculated solubility diagrams and the occasional absence of solubility data for Cs phases is not significant for real-world scenarios due to the high solubility of these phases in comparison to other salts.

The revealed discrepancies illustrate the need for further database work. Joint benchmark activities could help to identify missing or weak data, enhance the quality of all databases and consequently increase the confidence in modelling results.

The determination of homogeniety of geological reference material

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Reference materials (RM) support measurements in geological research due to the degree of homogeneity, traceability and confidence interval of their property values. Homogeneity testing is essential in certification of reference materials, as it should demonstrate the validity of the certified values and their uncertainties. Ingamells sampling theory [1] has been applied to test homogeneity of IAG Candidate RM trachyandesite (MTA), rhyolite (MRH), RM CGL MGL-AND andesite and uncertified USGS Granite (G-3). The sample digestion for test portions 50 mg to 500 mg was performed following the protocol [2] by sodium peroxide sintering and measurements with ICP-MS.

It is proposed that at least 300 mg is the minimum test portion size for trachyandesite (MTA) and Granite G-3 and 100 mg test portion for Rhyolite (MRH) and MGL-AND andesite to assure acceptable precision less than 2%. Complete digestion of all the analytes including mineral zircon is possible with sample/Na2O2 ratio 1:6.

In establishing reference values for reference materials, the contribution of detectable heterogeneity to the overall uncertainty of individual reference values has been quantified. The method has been developed to recover all analytes in particular zircon for 50 mg test portion size but it is suggested that 50 mg test portion is not representative for the particular rock types. It is also recommended to use ICP-MS as a tool of analysis as WD-XRF cannot determine homogeneity in specified test portion due to lower detection limits.

**Water storage in the Earth’s mantle**

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Experiments were performed under water-saturated conditions in the MFSH and MFASH systems as a function of pressure and temperature from 2.5 to 13.5 GPa covering the whole depth range of the upper mantle. Water contents were analysed by Fourier transform infrared spectroscopy \(^1\) and water values reported here use the new extinction coefficient for olivine \(^2\). The incorporation of Al enhances water incorporation in olivine and pyroxene, but only at pressures of 2.5 and 5 GPa. The partitioning of water between pyroxene and olivine is very high (4.4) at 2.5 GPa and below 1250°C, but decreases to an average value of 1.2±0.4 for higher pressures and temperatures. At 13.5 GPa and 1400°C, the water content of olivine is 1100±200 ppm wt H\(_2\)O. We conclude that the water storage capacity of the upper mantle just above the 410 km discontinuity can be anchored to ~900 ppm wt H\(_2\)O. If we interpret that the Low Velocity Layer observed near 350 km is due to mantle melting, we can constrain the water content of the mantle at that depth to be ~650±150 ppm wt H\(_2\)O. This new value is twice higher than previous estimates for the mantle source of Mid Oceanic Ridge Basalts but within the range of OIB sources.


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**Gujba age formation revisited : a possible use as time anchor**

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The meteorite Gujba is a primitive CBa carbonaceous chondrite (Bencubbin-type) that differs markedly from common chondrites. It displays a high metal abundance (metal/silicate ~1.7-3), a depletion in volatile elements, a quasi absence of CAIs and matrix, and large silicate chondrules (up to one cm) \(^1\). Metal and silicates are proposed to have both formed by condensation in a high temperature environment, as completely molten droplets and both exhibit quench textures. These features suggest a formation from a vapour-melt plume produced by a giant impact between planetary embryos after dust in the protoplanetary disk had largely dissipated \(^2\). This supposed formation in a single event followed by a rapid cooling predicts that all chronometric systems closed at the same time such that Gujba is an ideal candidate to anchor the short-lived chronometers onto an absolute timescale.

We have undertaken a project to date individual Gujba chondrules, using the precise assumption-free U-corrected Pb-Pb dating method \(^4,5\) to first confirm the single-event formation model and refine its absolute age.

Five cm-sized chondrules from a single slab of Gujba have been extracted and characterized by SEM. Three of them have been processed by a stepwise dissolution method \(^4\). Using a \(^{208}\text{Pb}-^{206}\text{Pb}\) double spike, we analyzed the Pb isotopic composition by thermal ionization mass spectrometry to obtain well-constrained internal isochrons on single chondrules. For now, ages were calculated using the \(^{208}\text{Pb}/^{206}\text{Pb}\) ratio of 137.786±0.013 that was determined by \(^5\) for inner solar system materials except CAIs.

Three chondrules have been dated with ages that range from 4562.61±0.28 to 4562.32±0.48 Myr, with a weighted average of 4562.52±0.44Myr. This is ca 1 Myr older than previously published absolute Pb-Pb age \(^2\), when it is adjusted for a U isotopic composition of 137.786. If the adjusted-age from \(^2\) is correct, this discrepancy could suggest different populations of chondrules within Gujba, which, in turn, requires a new formation model.


DOI:10.1180/minmag.2013.077.5.2

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Isotopic composition of water vapour in strong convective updrafts

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The isotopic composition of water is a tracer of interest for understanding convective processes, and the last decade has seen a surge of modelling and observational studies in that field. Yet, the physics of convective clouds governing the transformation of water across its different phases is potentially very complex and the exact dependence of isotopic compositions upon it is not well known nor has been extensively documented since the pioneering work of Jouzel et al. [1]. Important processes to consider include kinetic effects that arise from super-/subsaturated conditions due to liquid-ice disequilibrium in mixed phase zones and to lengthy phase adjustment over ice; isotopic re-equilibration between vapour and a variable reservoir of cloud liquid water; and different routes to cloud glaciation (freezing vs. the Wegener-Bergeron-Findeisen process). Using a simplified adiabatic model, we clarify the role of those processes in altering the isotopic composition of water vapour in strong convective updrafts.

We find that the deuterium-excess, which is the conventionally used metric of the joint distribution of deuterium and oxygen 18, is highly sensitive to cloud physics at low temperatures (< -30°C), with a complicated structure of variability resulting from multiple factors. We propose new metrics that relate deuterium and oxygen 18 isotopic ratios at cloud base and cloud top and that are better related to the structure of evolution of those isotopic ratios [2]. We show that, in a statistical sense, those metrics are respectively informative on the level of supersaturation reached by the cloud upon the completion of glaciation (which removes the control of saturation by liquid water); and on the temperature at which cloud glaciation is effective. The retrieved information can serve as a probe of the physics of deep convective clouds.


Early Eocene Climatic Optimum: numerical modelling of the impact of the Neo-tethys closure.

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The Early Eocene Climate Optimum (EECO, 53-50 Ma) was the warmest interval of Cenozoic time. This warm climatic interval was induced by a high atmospheric pCO2. Several mechanisms have been proposed to explain this climatic anomaly (e.g. LIP of North Atlantic). However one of them seems to be the most convincing in term of carbon fluxes degassing: the Neotethys closure, resulting in large amounts of pelagic carbonates recycled as CO2 in arc volcanoes during the subduction process. Hoareau et al. (submitted) [1] have modelled the volume of subducted sediments and the related amount of CO2 and CH4 emitted at active arc volcanoes along the northern Tethys margin. The volume of hemipelagic carbonates and the Indian continental margin carbonate sediments subducted, can produced a maximum of 3.7x1018 molCO2/Ma during the EECO, corresponding to a maximum of 85% of the modern CO2 outgassing rate. A numerical modelling has been performed to test the impact of these carbon fluxes on the climate using a model of biogeochemical cycles of carbon (COMBINE) coupled with a general circulation model (FOAM). Different parameters, as the size of Greater India continental margin and the timing of the continental subduction, have been tested in order to reconstruct the potential scenario which could occurred during this interval.

Highly variable $^{15}$N-enrichments in Solar System reflect different routes of interstellar N isotopic fractionation

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Large nitrogen (N) isotopic variations are observed in our Solar System ($^{14}$N/$^{15}$N ~ 50 to 450), with most of the objects being $^{15}$N-enriched compared to the presolar nebula (PSN, $^{14}$N/$^{15}$N = 442) [1]. We suggest that these variations originate from distinct sampled N interstellar reservoirs. Indeed, N-bearing molecules detected towards dark clouds may be divided into two groups, whether they carry the amine (-NH) or nitrile (-CN) chemical function. Our recent observations towards interstellar dense clouds, together with a review of data from the literature, suggest these two reservoirs are characterized by distinct isotopic ratios [2]. Compared to the PSN, (i) nitrile carriers (e.g., HCN) might be systematically enriched in $^{15}$N ($^{15}$N/$^{14}$N=100-320 and (ii) amine carriers (e.g., NH$_3$) are characterized by comparable isotopic ratios ($^{15}$N/$^{14}$N ~ 400). Gas-phase chemical networks suggest that nitriles derive from N while amines are formed via N$^+$, product of the dissociative ionization of N$_2$. The $^{15}$N-$^{14}$N exchange reactions are therefore different for nitriles and amines, most likely with different timescales and efficiency [2], explaining the differential fractionation of these two reservoirs.

The proposed scenario [2] appears to explain several observations on Solar System objects. In particular, the absence of significant $^{15}$N-enrichments in interstellar clouds, as previously assumed, is no longer a valid argument to reject an interstellar origin of organic precursors in primitive cosmomaterials.


A bimodal crystallite size distribution for mackinawite (FeS)

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The nanomineral mackinawite (tetragonal FeS, space group P4/nmm), ubiquitous in sulfidic sediments, impacts the cycling of metals and metalloids through sorption and reduction reactions. The crystallite size, hence the specific surface area, of FeS precipitated from supersaturated solutions is poorly described; variations in crystallite size may arise from differences in mineral synthesis conditions and from differences in measurement techniques used to estimate crystallite size. Transmission electron microscopy (TEM) images and X-ray diffraction (XRD) patterns have been used to study FeS crystallite size. However, XRD is sensitive to the largest crystallites and identification of small crystallites in TEM images can be difficult when the crystallites are embedded in a matrix of aggregated particles.

In this research, we employ a combination TEM, XRD, and Fe K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy to estimate the size of FeS crystallites formed under varying conditions of pH, ionic strength and reaction time. X-ray absorption spectroscopy is sensitive to the smallest crystallites, providing an estimate of size that is complementary to TEM and XRD. Furthermore, we calculate crystallite size distributions that are able to reconcile the XRD-, TEM-, and EXAFS spectroscopy-derived estimates of size. We suggest that the crystallite size may be bimodal, with a larger number of crystallites less than 2 nm in size than has previously been estimated using TEM and XRD. The presence of numerous small ($<$ 2 nm) crystallites will have large ramifications for the properties of FeS, including its solubility and the rate and mechanism of particle growth. Lastly, the crystallite size distribution can be used to inform studies of particle reactivity by constraining the reactive surface area and the number of surface sites.
Demixing instability in dense molten MgSiO₃

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The phase diagrams of MgSiO₃ and MgO are studied from first-principles theory for pressures and temperatures up to 600 GPa and 20,000 K. We present evidence for a vast pressure-temperature regime where molten MgSiO₃ decomposes into liquid SiO₂ and solid MgO. The demixing transition is driven by the crystallization of MgO - the reaction only occurs below the high-pressure MgO melting curve. The predicted transition pressure at 10,000 K is in close proximity to an anomaly reported in recent laser-driven shock experiments of MgSiO₃. We also present new results for the high-pressure melting curve of MgO and its B1-B2 solid phase transition, with a triple point at 327 GPa and 11,800 K. Comparison with experimental measurements and explanation of the observed phase boundaries in terms of the computed free energies will be discussed.

Clumped isotope thermometry of marbles as an indicator of the closure temperatures of calcite and dolomite with respect to solid-state reordering of C–O bonds

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Carbonate clumped isotope thermometry is based on the temperature-dependent preference of rare isotopes ¹³C and ¹⁸O to bond with each other within lattices of carbonate minerals (as measured by Δ⁴⁷ of CO₂ extracted by phosphoric acid digestion). In rocks that have experienced burial and/or high temperature histories, this phenomenon may be controlled by solid-state diffusion of C and O within the mineral lattice. Here we examine this issue through clumped isotope measurements of a variety of natural marbles that differ in metamorphic environment, age, cooling rates, grain sizes, and mineralogical and chemical compositions; and compare them to heating experiments conducted at laboratory timescales. Calcitic marbles increase in Δ⁴⁷ (by a range of ~ 0.05‰) with decreasing cooling rates (from ~ 100 to few °C/My), suggesting that ¹³C–¹⁸O reordering during cooling is controlled by solid state diffusion. Also, dolomite marbles are systematically lower in Δ⁴⁷ (by at least 0.06‰) than calcitic marbles, all other factors being the same. This does not appear to reflect differences between calcite and dolomite in the temperature dependence of clumping or the fractionation on acid digestion; rather, it appears that the blocking temperature with respect to solid-state ¹³C–¹⁸O reordering is significantly higher in dolomite (~300°C) than in calcite (~150-200°C), due to currently unknown chemical and/or structural controls.

These data are relevant for the use of clumped isotope thermometry to study deeply buried sedimentary carbonates and carbonate bearing diagenetic, metamorphic and igneous rocks. Perhaps most importantly, this work suggests that authigenic or early diagenetic dolomite may provide a means of recovering clumped isotope surface temperature records from even deeply buried sedimentary sections and sub-greenschist facies metamorphic rocks.
Underestimation of the authigenic fraction of Cu and Ni in organic-rich sediments and particles

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Organic-rich sediments from marine environments typically show authigenic enrichments in Ni and Cu. However, the exact determination of the authigenic metal level is difficult given the considerable level of the lithogenic metal background. The authigenic metal level can be estimated according to \( M_{\text{auth}} = M_{\text{total}} - \frac{M/Al_{\text{background}}}{Al_{\text{total}}}/M/Al \) while \( M = \text{metal of interest} \) and \( Al = \text{aluminum} \). Alternatively, a metal enrichment factor (EF) is calculated according to \( EF = \frac{M/Al_{\text{total}}}{M/Al_{\text{background}}} \). Both techniques rely on the appropriate use of the M/Al ratio of the lithogenic background. For the latter, the M/Al ratio of average shale or crust is widely applied as lithogenic background. Here, we show that the authigenic level of Cu and Ni in sediments and particles (upwelling areas of Peru, North and South Chile, Gulf of California, Norwegian Kylparen fjord and German Wadden Sea) is significantly underestimated when using the M/Al ratio of average shale or crust as lithogenic background. The correlation between Cu/Al and Ni/Al with organic carbon in the samples indicates the apparent M/Al ratio of the background, which is 2-4 times lower than the M/Al ratio of shale or crust. A prerequisite for our technique is high linearity and high quality of correlation (\( r^2 \geq 0.8 \)) otherwise the lithogenic background cannot be exactly determined. The resulting higher authigenic level of Cu and Ni underlines their use as productivity indicators in modern and paleo records while the enrichment of Cu and Ni shifts from moderate to high if it is assessed via EFs.

The stable chromium isotopic composition of Lunar basalts

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Planetary formation has been widely studied using major-element constituents of planetary mantles [e.g. 1]. The Moon’s formation is a highly debated topic and it has been proposed that the Moon is the result of a Mars-sized impactor which collided with the proto-Earth [2]. Non-traditional stable isotopes have been used to try to understand the formation of the Moon and its differentiation [e.g. 3].

Chromium isotopes are fractionated during core formation and differences in Cr isotopic composition between meteorites and the Earth’s mantle suggest that light Cr isotopes have been preferentially partitioned into the metal fraction [4]. Lunar samples are characterised by a lack of nucleosynthetic anomalies for Cr isotopes [5].

In the absence of samples from the Moon’s interior and in order to better constrain the lunar mantle composition and understand its formation we report stable chromium isotopic composition for a suite of low-Ti and high-Ti mare basalts. We find resolvable Cr isotopic variations within the lunar sample suite but no clear differences between low-Ti and high-Ti basalts. There is no correlation between \( \delta^{53}\text{Cr} \) and \( \delta^{18}\text{O} \). However, Cr isotopes seem to be correlated with Mg# and TiO₂ content which suggest that Cr isotopes are fractionated during magmatic differentiation on the Moon. The more primitive samples have Cr isotopic composition similar to the Earth’s mantle.

These results suggest that the terrestrial and lunar mantles have similar stable Cr isotopic composition. This implies that processes responsible for the difference in isotopic composition between the Earth’s mantle and chondritic material occurred before the formation of the Moon.


Fungi-mineral interface: hotspot of weathering in soils

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Throughout geological times, tectonic forces have continuously exposed rocks to the slow but inexorable actions of weathering at the Earth’s surface. This geological process forms soils upon which the entire terrestrial biosphere depends. Weathering of primary rocks also has a key-role in the carbon cycle as the alteration of Mg- and Ca-silicates coupled to the deposition in sediments of Mg- and Ca-carbonates results in a net flux of CO2 from the atmosphere to the lithosphere. Over geological timescales, this transfer controls atmospheric CO2 levels and hence the climate. Initially conceptualized in terms of abiotic dissolution reactions alone, there is now growing evidence that plants and their root-symbiotic partners, mycorrhiza, are key to the weathering because of their impressive capacity to interact physically and chemically with minerals.

In soils, mycorrhiza grow preferentially around, and on the surface of nutrient-rich minerals, making such contact zones potential hot-spot of mineral alteration. Here, we present a compilation of results and observations from alteration experiments in which ectomycorrhiza (Paxillus involutus) were grown symbiotically with a pine tree (Pinus sylvestris) in presence of freshly-cleaved biotite under humid, yet undersaturated, conditions typical of soils. Using FIB (Focussed Ion Beam), cross-sections of fungi-biotite interfaces were sampled along single, surface-bound hypha and analysed for (i) their contents in Si, O, Fe, Al, Mg and K at a nanometer-resolution (by STEM-EDS) and for (ii) the speciation of redox-sensitive elements (by STXM) [1]. In parallel to the biotite characterization, the chemical conditions in the near-environments of hypha and their biochemical composition were analyzed by molecular probes coupled to confocal microscopy and synchrotron-based μ-FTIR. This dataset shed light into mechanisms and also allowed for a first estimation of chemical alteration rates at the interface between fungi and rock-forming minerals [2].


XAS and isotopic approaches to identify Zn and Cu sources in the Seine River watershed

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In order to preserve the global freshwater resource, new directives on water policy have been established imposing a good ecosystem status for 2015. For the Seine-Normandie basin, it includes the metals sources determination in order to identify the metal amount resulting from the geochemical background, and the metal amount arising from industrialisation. The combination of isotopic and XAS approaches should allow to identify the different sources, and to understand the different processes controlling the Zn and Cu cycling. Variations on the δ66Zn and δ65Cu can provide information relative to the main sources of metals. XAS spectra study (through the knowledge of Zn and Cu speciation) is needed to understand the processes acting on the rivers (isotopic fractionation induced by biogeochemical processes [1,2,3] versus water mixing) and determine the bioavailability of Zn and Cu. As a potential Zn source, the sediment dynamics in the river have been investigated. To do so, sediment traps representative of river bottom sediments have been analysed using XAS at the Zn K-edge. In these samples, poorly crystallized Zn sulfides constitute the Zn major species, and could explain the presence of ZnS in suspended particulate material in the river water column. In addition, two “geographic” sampling campaigns have been performed to estimate the impacts of the different environmental conditions on the Zn/Cu signal, and to help locating the potential metal sources in the system. These two campaigns highlight a general seasonal effect linked to the discharge, in addition to punctual concentration anomalies.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Paroxysmal degassing at Mt. Etna in 2011-12

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Between January 2011 and April 2012, Mt. Etna produced a series of 25 paroxysmal lava fountaining events, representing a significant change in its eruptive style. Understanding the causes and impacts of this activity is crucial for improved hazard assessment at Etna, and for refinement of models of the volcano’s magma plumbing system. Sulfur dioxide (SO₂) emissions associated with most of these paroxysms were measured by the ultraviolet (UV) Ozone Monitoring Instrument (OMI) on NASA’s Aura satellite and the Atmospheric Infrared Sounder (AIRS) sensor on the Aqua satellite. The ground-based OPGC VOLDORAD 2B L-band Doppler radar system, operated in cooperation with INGV-CT, also detected the associated ash plumes, providing accurate constraints on the timing and duration of the lava fountains. We present a comprehensive analysis of the OMI and AIRS SO₂ data for the Etna paroxysms in 2011-12. Back trajectory analysis of the observed SO₂ clouds using the HYPLIT trajectory model indicates that SO₂ emissions generally coincided with the peak lava fountain intensity detected by the CF mechanism as the predominant driver for paroxysms at Etna in 2011-12. Satellite data indicate low or undetectable loadings also indicate a vast excess of gas in the emissions. Of the two models typically invoked for explosive basaltic eruptions (the rise speed dependent (RSD) and collapsing foam (CF) models [1]) we propose that our dataset supports the CF mechanism as the predominant driver for paroxysms at Etna 2011-12. Satellite data indicate low or undetectable ash content in the drifting eruption clouds, suggesting efficient separation of ash and gas in the eruption column, with implications for aviation hazards.


Dissolved gases and radioactivity in spring waters of southeast Brazil

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Twenty two spring water samples from spas located at São Paulo and Minas Gerais states, southeast Brazil, have been sampled and analyzed for temperature (T), conductivity (C), pH, redox potential Eh, dissolved gases O₂, CO₂, H₂S and radionuclides ²²⁸Ra, ²²⁰Rn and ²²²Rn. The samples provided by different geological contexts, i.e. Paraná sedimentary basin, Poços de Caldas alkaline massif and high grade metamorphic suites. The RAD7 portable detector (Durridge Co.) has been used for ²²⁰Rn and ²²²Rn analyses, as well traditional potentiometric/colorimetric methods and radiochemical steps followed by gamma ray spectrometry through NaI(Tl) scintillation detector.

The following data range has been found: T=21.7-28.4 °C; C=0.04-4.73 mS.cm⁻¹; pH=5.56-9.38; Eh=-115–122 mV; O₂ =1.3–9.0 mg.L⁻¹; CO₂=<1.0–800 mg.L⁻¹; H₂S=<1.0 – 3064 μg.L⁻¹; ²²⁸Ra=<5.4–123.2 mBq.L⁻¹; ²²⁰Rn=0.1–23.4 pCi.L⁻¹; ²²²Rn=0.6–2020 pCi.L⁻¹. Such great variability of values reflects the different lithologies, mineralogy of the rock matrices, discharge and climatic conditions, among others factors.

According to the Brazilian Code for Mineral Waters (BCMW) established by Register 7841 published on 8/8/1945, in terms of T values, the springs analyzed are cold (<25°C) and hypothermal (25-33°C). Several significant correlations were found involving the parameters analyzed, for instance: Eh and pH (r= -0.58), H₂S and C (r=0.64), T and ²²⁰Rn (r= -0.61), T and ²²²Rn (r=0.42), ²²⁰Rn and ²²²Rn (r= 0.59). Neither O₂ nor CO₂ and H₂S exhibited significant correlation with T, as expected, however, this scenario may modify if an expanded database including values for mesothermal, isothermal and hyperthermal waters is taken into account. According to the BCMW, in terms of radiological aspects, the springs analyzed can not be considered thoriferous as the ²²²Rn activity concentration is lower than 26.9 Bq.L⁻¹. One spring may be classified as weakly radioactive, as exhibited ²²²Rn activity concentration between 67.2 and 134.5 Bq.L⁻¹. Most of the ²²⁸Ra activity concentration data were below the detection limit, whereas one spring exhibited a value exceeding the guideline value of 0.1 Bq.L⁻¹ established by the Brazilian Health Ministry Register 2914 published on 12/12/2011. Therefore, the acquired data are relevant for the appropriate management and use of the studied spring waters.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Complexation of Sr in aqueous solutions equilibrated with silicate melts: Implications for fluid-melt partitioning

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Fluid-melt partitioning of Sr, Ba, La, and Y strongly depends on fluid and melt composition [1-2]. That is, partition coefficients of these elements increase with i) salinity of the fluid and ii) increasing alumina saturation index (ASI: Al/(Na+K) in moles) of the silicate melt (Fig.1).

On one hand, the distinct affinity for chloridic fluids points to a preferential complexation of these elements with chlorine. On the other hand, the strong dependence on melt composition suggests that a different release of melt components into the aqueous fluid in peralkaline systems changes the speciation in the aqueous fluid. Up to now, the exact nature of the complexation in the fluid is not clear.

Here, we present experimental and theoretical data on the complexation of Sr in three fluid-melt systems. X-ray absorption spectroscopy was applied to probe the local environment around Sr in silicate-bearing fluids, i.e., peralkaline or peraluminous melts completely dissolved in the aqueous fluid, and in various model systems, e.g., crystalline compounds, silicate glasses, and aqueous solutions. In order to decode the complexation of Sr in model systems and silicate-bearing fluids, theoretical spectra are calculated either using model structures, by testing several small cluster geometries or based on snapshots of trajectories produced with MD simulation to account for atom movements in aqueous solutions. Experimental data clearly show differences in the local environment around Sr in studied silicate-bearing fluids. Theoretical spectra point to a predominant formation of i) SrO₆ cluster in chlorine-free peralkaline fluids, ii) distorted SrO₆ clusters in chloridic-peralkaline fluids, and iii) complexes that very likely incorporate Cl⁻ in chloridic-peraluminous fluids.


Formation of arsenic bearing apatite from calcite. Chemistry and microstructures

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Apatite, a calcium phosphate mineral, can form naturally as solid solutions with between 0-100% of the phosphate anions substituted with compatible molecules in the crystal lattice [1]. Arsenate, AsO₄³⁻ is one such molecule, and there are many examples in nature of high As bearing apatite [2].

In order to track the chemistry of ancient fluids that formed the observed composition variation in apatite and related mineral deposits, a series of hydrothermal synthesis experiments were performed, aiming to establish a relationship between apatite composition and fluid chemistry. Utilising a general method from a previous study [3], we have generated a range of synthesised apatite samples starting from calcite, primarily by reaction with phosphate (PO₄³⁻), substituting with similar molecules (e.g. AsO₄³⁻, SO₄²⁻). Chemical analysis of thus formed apatite-like compounds show differing level of incorporation depending on the molecule being substituted, while SEM and CL mapping of grains show very interesting and complex textures and element distribution patterns. Two stage experiments, where one solution composition is reacted with pure calcite, then a different solution is reacted with the product, show that phosphate is an important driver for As-bearing apatite growth, and that arsenic incorporated into the apatite structure is not readily remobilised. This level of understanding is important when considering natural apatite samples as indicators to track ore fluids.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Meter-scale chemical interaction between pyroxenite-derived melts and mantle peridotites in the Northern Apennine ophiolites (Italy)

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Mantle peridotites from the Northern Apennine ophiolites are characterized by the occurrence of cm-thick pyroxenite layers originated by rather deep segregation of MORB-type melts. Our recent work documents that during the pyroxenite emplacement portions of the country peridotite have been significantly modified in their modal, chemical and isotopic compositions by reaction with melts percolating from pyroxenite veins [1]. Here we report the results of detailed bulk and mineral major and trace element profiles carried out through pyroxenite-peridotite boundaries to investigate the physico-chemical parameters governing the melt-rock reaction process. Relative to the peridotites far (> 2 m) from the pyroxenite veins, wall-rock peridotites show i) modal orthopyroxene enrichment at the expense of olivine, ii) higher Al, Ca, Sr contents and slightly lower Mg# iii) Al-richer spinel and lower-Mg# pyroxenes. Moreover, clinopyroxenes in the wall-rock peridotites have LREE-depleted patterns and initial εNd(430 Ma) = +4.7-+7.6, pointing to a reaction with an enriched tholeiitic silica-saturated melt. Along the pyroxenite-peridotite traverses, clinopyroxenes record a trace element gradient: at the pyroxenite contact they have the lowest MREE-HREE abundances, with lower Sm/Nd ratios than the distal pyroxenite-free peridotites. The overall REE abundances progressively increase away from the pyroxenite-peridotite boundary up to about 20 cm as a result of percolative reactive flow at decreasing melt mass. Beyond 20 cm from the contact, the HREE content decreases with distance from the pyroxenite, while the LREEs remain at nearly constant level, pointing to a more efficient chemical buffering of the host peridotite on the HREE composition of the percolating melt through ion exchange chromatographic-type processes.


How do organic molecules affect interactions of water with environmental sorbents?

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Water is the integral component of environmental phases and interfaces (e.g., in soils and sediments) and affects their structure and reactivity. Sorption interactions of water with environmental phases can be probed by their response to sorption of organic molecules. Such a test examines a sorbate hydration in a local microenvironment specific for a given probe. However, the direct measurement of the response of water-sorbent interactions to the presence of organic molecules at environmentally relevant conditions is difficult, due to typically low organic sorbate concentrations. Therefore, the use of the model-free thermodynamic approach [1] is proposed which allows determining the effect of organic compounds on sorbent-water interactions from the equilibrium sorption isotherms of organic molecules measured at varying water activities. The analysis included the data on (1) organic vapor sorption on such important soil components as minerals (i.e., quartz, clays, metal oxides) and organic matter (OM), and (2) the liquid phase sorption on the model soil OM. The amount of water expelled from a sorbent or co-sorbed, per an organic molecule sorbed, was obtained for different extents of sorbent hydrations. The water-expelling effect of organic molecules on minerals was analyzed by using Linear Free Energy Relationship (LFER). The LFER analysis suggested (i) the significance of organic sorbate polarizability associated with n- and π-electrons in driving water into the sorbent phase and (ii) the control of water driving-out effect by molecular size, H-bond acidity and basicity of sorbates. As distinct from minerals, water interactions with strongly hydrated OM phases (i.e., at water activities approaching one) become enhanced upon sorption of multiple organic sorbates containing oxygen, nitrogen or sulfur atoms. This OM hydration enhancement may involve several water molecules per a sorbed organic molecule and seems to be cooperative, which may need to be incorporated into models of organic compound sorption by soils and sediments. Importantly, this effect of the OM hydration enhancement suggests that a pre-hydration of OM does not necessarily create the OM configuration appropriate for further accommodation of other molecules.

57\textsuperscript{Fe} Mössbauer spectroscopy of pantelleritic melts

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Fe species in the melt can include 4-Fe\textsuperscript{2+}, 5-Fe\textsuperscript{2+}, 4-Fe\textsuperscript{3+}, and 5-Fe\textsuperscript{3+}. The relative proportions between these species can vary according to bulk glass composition and oxygen fugacity conditions, Red\textsuperscript{O}x state and coordination of Fe can considerably affect important physical properties (density and viscosity) of magma, even where bulk composition and Fe content are constant. A set of silicate glasses with pantelleritic composition have been synthesized at different oxygen fugacity conditions (from air down to IW buffer) and then were analyzed by 57\textsuperscript{Fe} Mössbauer spectroscopy (MB). The spectra were taken at 298K in transmission mode and fitted by applying an extended Voigt-based lineshape according to [1]. The MB spectra of all samples display three lines which can be described to two different doublets. One doublet with an isomer shift (IS) of ca. 0.9 mm/s relative alpha-iron and a quadrupole splitting (QS) of ca. 2 mm/s can be attributed to ferrous iron. The second doublet with IS of ca. 0.3 mm/s relative alpha-iron and QS of ca. 0.9 mm/s can be attributed to ferric iron. The later values are close to that of ferrous iron on tetrahedral site in ferrobasaltic glasses [2]. With increasing oxidation the QS of ferric iron increases slightly from 0.85 mm/s (0.3 Fe\textsuperscript{3+}/Fetotal) to 0.95 mm/s (0.8 Fe\textsuperscript{3+}/Fetotal) where a decrease of QS for ferrous iron as a function of oxidation was observed. The IS of 0.9 mm/s for ferrous iron remains constant up to an oxidation state of about 0.6 Fe\textsuperscript{3+}/Fetotal and with increasing oxidation a rapid decrease to IS of 0.6 mm/s at 0.8 Fe\textsuperscript{3+}/Fetotal occurs. At the oxidation state of 0.6 Fe\textsuperscript{3+}/Fetotal the constant QS of 2.0 mm/s for ferrous iron increases up to 2.45 mm/s at 0.8 Fe\textsuperscript{3+}/Fetotal in contrast to ferrobasaltic glasses, where a QS of 2.0 mm/s remains constant over the whole oxidation state [2]. Meanwhile, for tektites and alumino-silicate glasses [3, 4] the doublet with IS of 0.9 mm/s and 0.6 mm/s was attributed to ferrous iron on a five-fold and four-fold coordinated sites, respectively.


Luminescence products of hypergenesis ore deposits

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Luminescence analysis (L) can be successfully used in mineralogical studies of hypergene products. We studied the spectra of roentgenoluminescence (RL), and the thermoluminescence (TL) of minerals the oxidized zone Rubtsovsk deposit (Russia, Ore Altai). Found that the species composition of the loose mono and polymodal formations consisting of basic sulphate Cu, Pb, Al, and clay minerals can be determined from the characteristic spectra of RL and TL schedules. L studied minerals associated with defects in silicon-aluminum-oxygen tetrahedra, the excited states of oxygen and the presence of other native defects. Monoclinic dickite is diagnosed by the intense RL at λ = 350-360 nm, and very different from the triclinic kaolinite, which is characterized by weak luminescence in a wide wavelength range (285-300 and 340-350 nm). RL of kaolinite varies depending on the degree of crystallization and structural regularity. Halloysite is allocated by short-wave radiation with a peak in the spectral range 290-310 nm. In contrast to clay minerals alunite and osarizavatae spectra RL very low in intensity. Quantitative ratios of clay minerals and sulfates in their common units can be determined from the graphs of TL ignition minerals up to 450 °C.

Studied the L of hypogene and hypergene barite. RL spectra of barite formed in the oxidation zone differ from those of RH hypogene barite primary sulfide ore intense radiation in the wavelength range of 350-400 nm due to the excitation of oxygen. Thus, the study of products of hypergene luminescence methods allow: 1) to determine the degree of crystallinity of the mineral aggregates and order of the crystal lattice of minerals; 2) to use the luminescence for diagnostic purposes; 3) to solve individual genetic issues.

This study was funded by the Russian Ministry of Education and Science (projects 5.3143.2011, 14.B37.21.068, 14.B37.21.1257).

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Anthropogenic fractionation of zinc isotopes

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Zinc (Zn) is used in many industrial processes, including the galvanization of steel and the vulcanization of rubber. Due to its relatively low volatilization temperature, Zn is emitted to the atmosphere in greater quantities than any other trace metal worldwide. The fractionation of stable Zn isotopes during anthropogenic processing provides a potential opportunity to understand and evaluate the sources, transport, and accumulation of pollutant Zn in the environment.

Here we present the results from a series of investigations of Zn isotopes in anthropogenic systems, including a new investigation of lake sediment cores from seven urban lakes and one reference lake in the USA. The time-resolved records of sediment (and Zn) accumulation suggest that, on average, the $\delta^{66}$Zn (measured relative to JMC 3-0749L) of Zn from sediments deposited during intense urbanization is $0.09 \pm 0.07\%$ (n = 12), while the average isotopic signal for sediments deposited prior to urbanization (and in the non-urban reference lake) is $0.33 \pm 0.07\%$ (n = 23). The anthropogenic isotope signal for Zn fits well with previous investigations of Zn processing related to combustion, which may suggest that automobile emissions and waste burning are important contributors to urban Zn pollution. The natural background isotopic signal of Zn for lake sediments is similar to that reported for many igneous rocks. This may suggest that processes like weathering, transport, and biological uptake do not appreciably change the isotopic signature of the natural lake sediments.

This lake sediment study, as well as previous investigations of Zn-contaminated sediments, water, and atmospheric particles confirm that Zn isotopes can be useful to help distinguish between natural and anthropogenic Zn sources. However, because of the small amounts of fractionation and overlapping isotopic signatures, Zn isotope investigations are most successful when they are combined with other chemical and/or isotopic measurements.

Antigorite dissolution rates as a function of pH at 25 and 80 °C

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Antigorite (Mg$_3$Si$_2$O$_5$(OH)$_4$) is a common serpentine mineral that could provide the divalent metal cations required for mineral carbonation as part of carbon storage efforts. Such carbonation could occur via the dissolution of acidic CO$_2$ saturated H$_2$O. Antigorite dissolution into this fluid would both release aqueous Mg and neutralize the fluid promoting carbonate precipitation [c.f. 1].

In an attempt to better quantify this carbonation process antigorite dissolution rates have been measured as a function of pH from 2 to 10 temperatures of 25 and 80°C in closed system reactors. Rates were calculated from measured aqueous Mg and Si concentrations

$$r = \frac{(dC/dt)v}{S}$$

where $r$ is the dissolution rate, $dC/dt$ is the time derivative of Mg or Si concentration, $v$ is the fluid volume in the reactor and $S$ is the surface area.

Magnesium is released preferentially at the beginning of most of the experiments compared to silica suggesting the importance of Mg for proton exchange reactions in the antigorite dissolution mechanism. Also similar to the behavior of other Mg-silicate minerals including talc and tremolite [2], antigorite dissolution rates decrease systematically with increasing pH over the whole pH range considered in this study; antigorite dissolution rates at pH 2 are ~1.5 orders of magnitude faster than corresponding rates at pH 10. The addition of ~0.1 mol/kg citrate to the aqueous fluid appears to increase constant pH rates by less than an order of magnitude suggesting that the addition of organic ligands would be an inefficient method to accelerate the carbonation of Mg silicate minerals.

Insights on the protracted evolution of the deep crust of the Arabo-Nubian Shield.

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The Arabian-Nubian Shield (ANS) represents a mosaic of more than 15 Neoproterozoic juvenile island-arc terranes (850-600 Ma) formed in the Mozambique ocean realm. In spite of amalgamation events that subsequently led to accretion of the ANS, most exposed terranes are characterized by low- to moderate metamorphic overprint, greenschist-facies rocks being prevalent in the shield. It is thus difficult to examine how and when the lower crust of the ANS formed since it is mostly inaccessible. In this study, we analysed 3 gneisses from Zabargad Island (Egypt) corresponding to lower crustal units exposed at surface level during the Oligo-Miocene thinning of the ANS lithosphere related to the Red Sea rifting. Zircons from a felsic granulite have both low and high Th/U ratios (0.3 and 0.07), but yield undistinguishable ages of 652 ± 10 Ma, which we interpret as dating the age of the protolith and its conversion to granulite. Some zircons however yield low Th/U ratios and a significantly younger age of 597 ± 4 Ma, reflecting a second metamorphic event, possibly related to collision between island arc terranes of the ANS and the Saharan craton on the West. Monazites from a granulitic gneiss yield a much younger age of 497 ± 2 Ma which may reflect far-field stress associated to the latest stages of amalgamation of eastern Gondwana. Lastly, zircons extracted from a granulitic gneiss sampled at the contact with the Northern peridotite massif yield an age of 25.1 ± 0.4 Ma related to contact metamorphism during juxtaposition of the hot peridotite and lower crustal units. Gneisses from Zabargad island constitute a unique window to look at the polymetamorphic evolution of high-grade lower crustal units of the ANS.

Micro-fracturing induced by radioactivity of minerals: consequences on the permeability of rocks.

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Some rocks may contain radioactive (U-Th) minerals ranging from micrometric to millimetric sizes. These minerals are submitted to intense self-irradiation (α-decay of U and Th chains) that can lead to amorphization and also modify their environment by irradiating the host minerals. Amorphization induces volume increase, leading to the formation of cracks which eventually connected into a network through the rock. This fracturing allows fluid circulation, and promotes alteration of source minerals and dispersion of elements (e.g. Pb and U). These observations highlight the importance of understanding the impact of radiation damage on radioactive transport by fluids passing through such fractured rocks. The aim of this study is, through the caracterization of natural samples, to explore the consequences of such fracturing on the ability of rocks to transfer radioactive elements within fluid phases. The study was made up of imaging, laboratory measurements and numerical modelling.

First, the permeability of natural rocks with high-level of radioactivity, was measured. Such low permeability needs the use of specific gaz-permeameter. In agreement with the Klinkenberg effect, permeability of the samples can be obtained.

In a second step, these results were compared with those from numerical modelling. For that, the geometry of a micro-fracture network was used after SEM image processing. The model simulates both the flow in the fractures and the reactive transport associated with the dissolution of the radioactive minerals and helped us to evaluate the flow and the transport heterogeneity in a natural sample, induced by this local fracturation surrounding radioactive minerals.

For a better understating of this process, the use of X-ray CT-scan is necessary to develop a 3D model.
Carbonation of serpentinite mine tailing: the example of Montecastelli mine (Tuscany, Italy)

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Carbonation of serpentinite or asbestos mine tailing is a passive, weathering-related process that take advantage of the thermodynamically driven natural transformation of ultramafic rocks into carbonate and thus it is cost and energy effective. The enhancement of this natural weathering is a challenge including multiple advantages: CO2 capture, and remediation of asbestos tailing. Here, we present an example of natural carbonation of a small mine dump at Montecastelli (Tuscany, Italy).

At Montecastelli (Tuscany, Italy), a pluri-kilometric body of serpentinite, embedded in shales, has been deeply eroded by the Pavone River providing good exposures and sections. The central portion of the serpentinite body host a small copper ore deposit that was intermittently exploited during the XIX century, and was definitively closed in 1869. Bornite, chalcopyrite, chalcocite and pyrite veinlets and nodules, in a chlorite-serpentine-brucite-amphibole soapy gangue, characterize narrow deformation zones crosscutting the serpentinites. Most of the low-grade Cu-ore extracted in the past was not reliable for industrial processing and directly dumped in front of the entrances of the mine, forming by the time a small mining dump. Mining activity stopped 60 years ago.

Intense natural carbonation produced crust of hydrated Mg-carbonates (hydromagnesite, nesquehonite, manasseite, pyroaurite, brugnatellite) coating the serpentinite clasts of the mining dump and the serpentinite walls of the mine tunnels.

The Montecastelli carbonated serpentinite mine tailings represent an example of rapid atmospheric CO2 uptake. Their study improved our knowledge of the carbonation processes. Future quantification of the amount of carbon sequestered in geologic samples from Montecastelli would give an estimate for the sequestration capacity of ultramafic mine tailings in general and will provide a framework for the development of standard protocol for enhanced mineral sequestration at mine sites.

The Behavior of Beryllium in Soils and Aquatic Environments

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Beryllium is an important metal utilized in a diverse range of applications. Aside from its numerous industrial uses, it is as a central tool used in the field of geochronology and geomorphology. Recent work indicates 9Be leached from mineral lattices during weathering processes moves through a landscape adsorbed to soil particles and in solution. As such, the flux of 9Be from rivers is indicative of the weathering extent of soils within the catchment. Another isotope, cosmogenic 10Be, is formed in the atmosphere and is precipitated onto the Earth’s surface, adsorbing onto surface sediments. The concentration of 10Be in soils and sediments scales with the residence time of sediments in a landscape. Although these applications are dissimilar, they require an understanding of the behavior of beryllium in soils and aquatic environments. A better understanding of the mobility of beryllium will help constrain its use for such geologic techniques.

In order to evaluate the interactions of beryllium with soil and aquatic related materials, we selected model organic compounds and minerals to perform distribution coefficient experiments. Model organic compounds such as graphite, cellulose, an amine compound and phenolic acid in addition to dissolved organic matter samples were selected on the basis of their chemical composition and potential ability to adsorb beryllium. Clay-sized fractions of montmorillonite, illite, kaolinite and hectorite were also selected. The retention of beryllium onto each of these compounds was evaluated over a pH range and various equilibration times to determine which conditions allowed for the greatest retention of beryllium. Preliminary results conclude that mineral compounds more efficiently adsorb beryllium relative to the selected model organic compounds. Retention of beryllium increases with increasing pH from 2 to 6. We also examined the effect of pH on the speciation and colloidal nature of beryllium. For beryllium concentrations typical of natural soil solutions, we find that the colloidal behavior of beryllium may play a significant role in its mobility within soils.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Determination and quantification of fatty acids in speleothems and cave drip water using HPLC-ESI-IT/MS

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Cave drip water, speleothems and the proxies preserved within them have significant potential to record palaeoenvironmental changes in the regional vegetation [1]. The most common proxies measured in stalagmites are inorganic proxies, in particular oxygen isotopes [2]. More recently the importance of organic matter analyses in this field is examined. This study focuses on the research of lipid biomarkers. The lipids contained in stalagmites originate from the overlying soil and different plants, bacteria and fungi. Therefore different compositions of lipids may provide records of environmental changes [3].

In the following the development of a new method for the extraction of fatty acids (FA) from stalagmites and cave drip water and their measurement by HPLC-ESI-IT/MS (high performance liquid chromatography coupled to electrospray ion trap mass spectrometry) is presented. Five different FAs with chain lengths from C12 to C20 were applied as analytical standards. A mixture of these was used to optimize the separation by HPLC. The FAs were measured in negative polarity, so a time consuming derivatization of the analytes was not necessary. To simulate the extraction of the FAs from stalagmites and cave drip water several spiking experiments were performed. Solid phase extraction and liquid liquid extraction were used for the extraction procedure. Both methods were optimized and good reproducibilities with deviations below 10% were achieved. Quantitative analyses were accomplished and the limits of detection determined. As a proof of principle, first applications to the actual samples were successfully fulfilled.

To testify the role of the FAs as palaeoclimate proxies further applications to the actual samples were successfully fulfilled. Quantitative analyses were accomplished and the limits of reproducibilities with deviations below 10% were achieved.

Sub-micrometer scale chemical mapping of complex monazites: the contribution of the NanoSIMS.

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Monazite [(Ce,La,Nd,Th)PO4] is a very robust geochronometer which can record and preserve U-Th-Pb ages in various geological environments. For around ten years, monazite has also been increasingly studied because it is a key tracer for geological processes, especially fluid/rock interactions. Monazite grains often display variable chemical compositions at the grain scale and complex chemical zoning, sometimes correlated to age domains, reflecting the changes in physical and chemical parameters of the host rock. The development of in situ techniques (EMPA, LA-ICPMS, SHRIMP) enables the combined study of chemical and isotopic characteristics in the monazite at the scale of few µm. However, many recent studies show that: (1) it is not always possible to correlate age and chemical domains at these scales, (2) monazite often display very complex chemical zoning at infra µm scale and (3) TEM analyses show strong perturbations of the crystal lattice between 10 and 200 nm. In order to better understand the ages recorded by monazite it is necessary to obtain chemical informations at nm scale. In this context, the NanoSIMS appears to be the best suited tool.

We present here chemical elements (89Y, 139La, 208Pb, 232Th and 238U) NanoSIMS images and analyses obtained in monazites studied in thin section or separates. 89Y, 139La, 208Pb, 232Th and 238U ion images were obtained in monazite areas previously studied with EMPA and dated with LA-ICPMS. The NanoSIMS maps allow to characterise isotopically and chemically distinct domains that were not distinguishable on WDS X-ray maps. 206Pb/238U maps derived from NanoSIMS images offer the possibility to correlate different age domains with the measured 206Pb/238U ages obtained at larger scale (few µm) by LA-ICPMS.

These results are very promising for compositional and isotopic mapping with a highest spatial resolution in the monazite geochronometer.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Simulation of physical and chemical processes of polluted air masses during the Aegean-Game airborne campaign using WRF-Chem model

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The chemical and dynamic processes as well as the atmospheric composition, in the Planetary Boundary Layer (PBL) over the Aegean Sea, are investigated during an ‘Etesian’ event (29/8-9/9/2011) based on modeling results and a combination of airborne and ground observations. During this period atmospheric parameters, concentrations of gaseous species and size-resolved aerosol chemical composition have been measured using instrumentation flown on the UK’s BAe-146-301 Atmospheric Research Aircraft operated through FAAM [1,2]. The simulations were performed by the on-line meteorological and chemical transport WRF-Chem model. Anthropogenic and on-line calculated natural (biogenic, sea-salt) emissions have been considered. Fire emissions generated by the FMI Fire Assimilation System [3] have been also included. The horizontal and vertical distribution of gaseous and aerosol species is interpreted in relation to the evolution of the PBL, and is shown that the model captures the geographical and temporal variations observed.


Polyoxometalates and Their Effect on Tungsten Speciation and Transport

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Tungsten (W) is a toxic element with complex aqueous speciation. Tungstate, W(VI), is the dominant oxidation state of tungsten in soils, forms a variety of insoluble tungstate minerals, and often adsorbs strongly to iron oxides. This W(VI) often is significantly more readily transported than expected based on the available thermodynamic data. We have examined the role of metastable and polyatomic polyniobates in enhancing the solubility of tungsten in natural systems. We have measured W concentrations following reaction with model soil minerals, and natural soils, over a variety of solution compositions and reaction periods in which a variety of polyniobate species may form in solution. In particular, we examined the effect of initial W(VI) concentration and speciation, pH, and the presence of silicate and phosphate on W(VI) sorption. The speciation and structure of adsorbed W(VI) on ferrihydrite also were examined using synchrotron-based X-ray absorption spectroscopy (XAS). Adsorption isotherms and envelopes show a complex relationship between pH and W(VI) adsorption, with more W(VI) retained at circumneutral pH. Adsorption was less extensive in solutions containing more polymeric species, suggesting that these species do not adsorb to ferrihydrite surface as strongly as does the tungstate anion. Polyoxometalate (POM) clusters form in the presence of phosphate, or persist as metastable complexes for sufficient duration to considerably enhance the solubility and transport of tungsten in natural environments. XAS confirmed that tungstate usually represents the bulk of adsorbed W(VI), but polyniobates also appear to be adsorbed to the mineral surface, particularly in systems in which W(VI) was most soluble. Equilibrium adsorption onto ferrihydrite was not achieved and takes more than one month; this unusually slow adsorption is due to the slow decomposition of weakly-adsorbing polyatomic anions to monomeric tungstate anions. The kinetic stability of metastable polyniobates thus may further enhance W solubility in natural waters and its migration in natural environments.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Relating U-Th-Pb ages of accessory minerals to metamorphism: A case study from the Barrovian sequence of the Central Alps, Switzerland

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Accessory minerals allanite, monazite and rutile from amphibolite facies rocks across the Barrovian sequence of the Central Alps (Switzerland) were investigated for composition and U-Th-Pb ages. The growth ages of these minerals record stages of prograde and peak metamorphism.

Allanite formed during the prograde path at 26-33 Ma. It occurs aligned along an early foliation that is overprinted by later generations of mica. In some cases, the foliation along which allanite is aligned is only preserved in garnet. Rutile from one metapelite in the central region also records a ~33 Ma age. Zr-in-rutile thermometry yields a temperature of 550±20°C, which is lower than the 620°C peak temperature deduced from the main mineral assemblage [1], indicating that rutile crystallised under prograde conditions. We interpret this early age as the time when the rocks reached peak pressure conditions.

The timing of peak temperature conditions is recorded in monazite, rutile and, in one sample, allanite rims. Monazite yields an age of 22 Ma and grew at the expense of allanite and after the first stage of garnet growth. In monazite-bearing samples, allanite is preserved as inclusions in garnet, whereas monazite is part of the matrix. Zr-in-rutile thermometry suggests that 23 Ma rutile in a calcschist records the timing of peak temperature conditions. 20 Ma allanite rims in one metapelite crystallised on older (27 Ma) cores, and are also interpreted to reflect the timing of peak to retrograde conditions.

Through multi-mineral geochronology a prograde metamorphic history, spanning some 10 Ma, can be reconstructed: from prograde greenschist facies to peak amphibolite facies conditions. The observation that 33 Ma prograde rutile is preserved despite the later temperature peak at 22 Ma suggests a closure temperature of Pb in rutile in excess of 620°C.


A multi-isotope (H, O, C, S, B, Mg, Ca, Ba) approach to study diagenesis in Black Sea-type sediments

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Like The Black Sea, The Baltic Sea Has Switched Between Fresh Water And Brackish Water Modes. The Changes In Paleo-Environmental Conditions Caused Downcore Gradients In The Concentrations Of Dissolved Species In The Pore-Waters With Consequences For Microbial Activity And Physicochemical Water-Solid Interactions Associated With Multiple Stable Isotope Fractionation Processes. Here, We Introduce A New Combined Multi-Isotope And Trace Element Approach To Investigate Diagenesis In These Non-Steady State Systems.

In a Gotland Basin core, it is found that concentrations of conservative elements and the pore water H-2 and 18-O contents decrease with depth due to diffusion from brackish waters into underlying fresh waters. A downward increase and decrease of Ca and Mg concentrations, respectively, is associated with decreasing Ca-44 and Mg-26 isotope values. B-11 isotope values decrease in the limnic part. An increase in Ba concentrations with depth is associated with a slight increase in Ba-137/134 isotope values. Microbial activities lead to an increase in DIC, but a decrease in SO4 concentrations and in C-13 contents of DIC with depth. Desorption of Ba from glacial sediments due to downward diffusing ions is responsible for the formation of sedimentary barites. S-34 and O-18 isotope values of barites suggest that these were formed in glacial sediments from pore waters strongly depleted in O-18. Impacts of diagenetic processes on multi-isotope signals in pore waters and authigenic phases are discussed. Mixing between brackish and fresh waters, solid-liquid interactions, and transport reactions explain most of the observed isotope variations along the vertical pore water profile.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
High Velocity Collisions Recorded in Asteroidal Meteorites: New Ways to Constrain Planet Formation

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It was recently shown that 40Ar–39Ar ages in meteorites reflect unusually high impact velocities exceeding 10 km/s [1]. Compared with typical impact velocities for main-belt asteroids of about 5 km/s, these collisions produce 100–1,000 times more highly-heated material by volume. It was proposed that the 40Ar–39Ar ages between 3.4 and 4.1 Gyr ago from Vesta, the H-chondrite parent body and the Moon record impacts from numerous main-belt asteroids that were driven onto high velocity and highly eccentric orbits by the effects of the late migration of the giant planets. The timing of these asteroidal and lunar impact signatures help define the so-called Late Heavy Bombardment.

An intriguing implication of this work concerns the 40Ar–39Ar events seen between ~4.4–4.53 Gyr ago among many stony meteorite groups. Although some of those ages may reflect cooling through the blocking temperature after igneous crystallization, others are unambiguously related to early impact events on primordial asteroids during the planet formation era [e.g., 2]. More recent impacts in the main asteroid belt ejected this material off the parent body, allowing it to reach Earth through dynamical processes. We postulate that these early high-velocity impacts likely came from leftover planetesimals residing in the terrestrial planet region, many of which had highly eccentric and inclined orbits. If true, these ~4.5 Gyr ago events constrain the nature and decay rate of this putative population, as well as early planet formation processes. Using numerical simulations, we will explore the implications of these results in our talk. We will also probe how these same methods and data allow us to glean insights into the timing of the giant impact that formed the Moon.


Hypersaline volatiles in a palladium-enriched mafic pegmatoid from the 2.48 Ga East Bull Lake intrusion, Sudbury District, Ontario, Canada

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The East Bull Lake intrusion (EBLI) is a Paleoproterozoic mafic-ultramafic (low-Ti, high-Al tholeiitic) intrusion located roughly 90 km west of Sudbury, ON. The intrusion itself consists primarily of massive- and layered leucogabbro and leucogabbronorite and is interpreted to be the product of crystallization of partial melts from sublithospheric depleted mantle, a remnant of a ~2.48 Ga large igneous/metallogenic province. The heavily contaminated lower zones of the intrusion host disseminated-blebby PGE-Cu-Ni sulfide mineralization (up to ~10s ppm PGE locally in massive sulfide pods).

Microthermometry was conducted on fluid inclusion assemblages containing late-stage magmatic-hydrothermal fluids in interstitial quartz from a mineralized pegmatitic leucogabbro from the central portion of the intrusion. The FIAs contain three-phase liquid-rich inclusions with halite daughter phases. Final homogenization occurred by halite dissolution at temperatures significantly higher than vapour bubble disappearance. Using a method for calculating minimum trapping pressures at the T of homogenization [1,2], FIAs not influenced by post-entrapment modification show minimum trapping pressures from 1.6-3.0 kbars, with final homogenization temperatures ranging from 291°C to 367°C (bulk salinities of 38-44 wt% NaCl equiv.). For comparison, Ti-in-quartz thermometry for fluid inclusion-rich domains in the quartz indicate crystallization from 650-750°C. The data suggest that if the inclusions are primary then actual trapping pressures are significantly higher than the minimum values estimated above, constraining the depth of emplacement of the mineralized intrusion to at least 18km.

The study provides first constraints on the nature of late-stage magmatic-derived fluids associated with the EBLI and provides a means for comparison to other mineralized intrusions that show involvement of magmatic fluids in the redistribution of chalcophile/highly siderophile ore metals.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Deep crustal melting revealed by Pb isotopes and seismology in the western US


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In comparison to the uniform coverage of the western US (WUS) provided by the USArray, the NAVDAT database shows many poorly sampled regions. We therefore measured the Pb isotope compositions of crustal xenoliths from numerous volcanic and plutonic rocks across the Colorado Plateau (CP), and also sampled felsic plutonic rocks outcropping east of it, where the crust have been particularly scarce. When possible, we separated low-U/Pb K-feldspars to obtain the Pb isotope composition of the host magmas. We combined our new data with literature Pb isotope data from ores and felsic plutonic rocks, all of which cast doubt on the geochemical and seismological variables of Pb model ages, U/Pb, and Th/U. (1) Pb model ages match geological ages only into the geologically informative variables of Pb model ages, U/Pb, and Th/U using a two-stage model. These parameters were then imaged on isotopic maps of the WUS using grid-cell averaging. Comparing the isotopic maps to seismic maps shows many poorly sampled regions. We therefore measured Pb isotope compositions of crustal xenoliths from numerous volcanic and plutonic rocks across the Colorado Plateau (CP), and also sampled felsic plutonic rocks outcropping east of it, where the crust have been particularly scarce. When possible, we separated low-U/Pb K-feldspars to obtain the Pb isotope composition of the host magmas. We combined our new data with literature Pb isotope data from ores and felsic plutonic rocks, all of which cast doubt on the geochemical and seismological variables of Pb model ages, U/Pb, and Th/U. (2) While U/Pb systematics, which are high in the Snake River plain, in Northern Utah, along the Uinta Mountains, along the western rim of the CP, and along the Rio Grande Rift, and in the Laramide uplifts in Colorado, all places where Vp/Vs is high, and represent regions of either crustal thinning or basement exposure. We suggest two scenarios: (1) The Th/U systematics, which are not visibly controlled by heat flow, attest to thinning of the local continental crust above hot mantle. Lateral removal of the upper and middle crust, by extensional faulting or channel flow, allowed the uplift of deep high-Th/U crustal rocks and their melting. (2) Exhumation of basement rocks by either deep-seated Laramide style thrust faults or as metamorphic core complexes provides access to deeper levels of the crust, providing the observed high Th/U values.


Large river floodplains: weathering without erosion?

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On their journey to the ocean, large river sediments undergo a series of sedimentation, temporary storage and reworking episodes in active floodplains, in which time is available for sediments to mature chemically. Weathering affecting material eroded from tectonically active mountain belts in these flat, non-erosive areas is a potential mode of coupling between erosion and weathering fluxes at the continental scale. We quantified the chemical fluxes associated with weathering of sediments in the floodplains of the Amazon and Ganga river systems [1,2]. To this end, river sediments were sampled upstream and downstream four river reaches across these basins. Sampling along depth-profiles grants access to the whole grain size and chemical composition range of river sediment. Weathering intensities of major elements (i.e. losses of Na, K, Mg and Ca) associated with chemical weathering in floodplains were examined as a function of grain size and integrated over the entire grain size range. Finally, we computed weathering fluxes, using a steady-state mass balance model at the scale of the river reach.

Across the four river reaches (Marañon, Beni, Madeira, and Ganga rivers), two consistent features emerge: (1) significant carbonate dissolution and subsequent Ca and Mg release to the dissolved load; (2) retention of K and Mg in the silicate phase of the sediment. These observations are in agreement with what is predicted from mineral kinetics. In this respect, sediment transport time across the river reach is a controlling factor on the floodplain weathering flux. However, across the studied river reaches, the variable extent of Na and Ca release by plagioclase dissolution points at an additional control on the intensity, namely the potential exhaustion of weatherable minerals before the sedimentary material enters the floodplain (be it in modern soils of the erosive area, or during ancient weathering episodes).

Altogether, our results show that floodplains constitute the predominant locus of weathering in the Gangetic system but not in the Amazon Basin. However, CO₂ consumption fluxes associated with silicate weathering in floodplains in these two river basin floodplains is on the order of magnitude as those resulting from weathering in their erosive areas.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Biogeochemical responses to gamma irradiation treatment of Alberta oil sands fluid fine tailings

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Exploitation of the oil sands in Alberta has created large volumes of waste materials termed fluid fine tailings (FFT). These materials are stored in large settling basins to allow adequate separation of the oil sands process water and the FFT. The separated water in these holding areas are used either for future processing or it is allowed to settle before reclamation into functional wetlands and end pit lakes. A major concern is the presence of Naphthenic Acids (NA); these are a toxic, recalcitrant group of carboxylic acids naturally released from bitumen during the extraction process. An unexplored treatment option to promote or speed the degradation process and reduce in situ effects of NA’s is gamma irradiation. In this study we examined the development of chemical REDOX gradients; and kinetic responses of indigenous microbes inoculated into irradiated FFT material using laboratory microcosms.

The systems will be set up using representative young and aged FFT material in both oxic and anoxic environments. Temporal changes to porewater and headspace water geochemistry was tracked along with in situ microsensor profiles and microbial community succession patterns. These results will have implications in development of a model framework to optimize treatment based on biogeochemical responses to waste type.

Closed system vs. open system degassing: a combined textural and geochemical approach

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Eruptive styles of volcanoes span a wide range of dynamic, from effusive to explosive. They depend on the magma composition, the volume of ejected magma and the magma ascent conditions in the conduit, from the reservoir to the surface. Magmas with the same composition and pre-eruptive conditions can generate different eruptive styles (eg. multistyles eruptions) evidencing the dominant effect of the ascent conditions of magmas. Understanding the behavior of the volatile phase in relation with the rheology of the magma (viscosity) during magma ascent is one of the main stake.

A detailed study of the textural characteristics (vesicularity, microcrystallinity) of the products of explosive eruptions associated to their composition and volatile content (pre-eruptive and residual) allow to better define the relations between the magma behavior in the upper part of the conduit and the eruptive style. In low-viscous basic magmas, pre-eruptive volatile content is low (2-3 wt%) and bubbles move independently in the melt, with a higher ascent velocity. Their coalescence forms large bubbles that blow up at the surface: the explosivity is low (strombolian eruptions). On the contrary, in high-viscous differentiated magmas, the pre-eruptive volatile content is high (up to 5-7 wt%) and bubbles display generally the same ascent velocity. The magma reaches the surface with a large proportion of bubbles (up to 75vol%) as an unstable foam, the fragmentation of which generates a high explosivity (plinian to vulcanian eruptions). In some cases, with similar magma composition and volatile content, part of the volatiles may escape through permeable conduit walls generating a bubble flattening and melt microcrystallisation, which in turn increase the magma viscosity, decreasing its ascent rate. At the vent, this magma is partly degassed with a very low explosivity potential (dome-forming eruptions), excepting some particular cases. All intermediate eruptive style exist between high and low explosivity, depending of the behavior of the magma during its ascent in the conduit.

We’ll discuss all these cases including the extremes and unusual cases as basaltic plinian eruptions or explosive dome-forming through several examples taken in recent eruptions.
Thermodynamics of Lower Mantle Minerals

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There is a general consensus that the Earth’s lower mantle is mostly composed of (Mg,Fe)SiO3 perovskite (Mg-Pv) and (Mg,Fe)O ferropericlase (Fp). Knowledge of the chemical and physical properties of these minerals is, therefore, essential for understanding the structure and dynamics of the lower mantle.

In this work, we performed a new compression study of Mg-perovskite (MgSiO3) and periclase (MgO) phases synthesized at variable conditions of the Earth’s lower mantle by using pure Mg2SiO4 as a starting material. In our experiments a Double-sided Laser-Heated Diamond Anvil Cell at the ESRF – ID27 (Grenoble) was used up to 100 GPa and 3000 K. The equation of state (EOS) at various conditions of P and T for Mg-Pv and Fp were obtained by integrating the available experimental data into a single P-V-T EOS to constrain the elastic parameters (bulk modulus, densities, etc …) under conditions of the Earth’s lower mantle, which provides a basis for evaluating the compositional models of the Earth’s lower mantle.

In this study, we will also combine our new results and the existing data in the literature to discuss and compare the combined effects of Fe and/or Al on the EOS of both phases and the chemical constraints that we can obtain from such comparisons. Finally, we will discuss our results on the light of the most recent studies on the melting curves of the lowermost Earth’s mantle and the stabilization of the ultra-low velocity zones associated with partial melting at the core-mantle boundary [e.g. 1-3].


C and O isotope compositions of the Matongo carbonatite (Burundi) : new insights into alteration and REE mineralization processes

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The Matongo carbonatite intrusion is part of the Neoproterozoic Upper Ruvubu alkaline plutonic complex (URAPC), located in Burundi along the western branch of the East African Rift. This alkaline complex, which also comprises feldspathoidal syenites, diorites, quartz-bearing syenites and granites, emplaced around 750 Ma [1].

Most of the oxygen and carbon isotope compositions obtained on the several carbonatitic facies are typical of carbonatites: the δ18O values are between 7.2 and 8.5‰ (vs. SMOW), the δ13C value are between -4.7 and -5.4‰ (vs. PDB). These values correspond to the magmatic signature of the intrusion. Some samples show a significant increase in the δ18O value, between 11 and 20‰, with an extreme value of 21.6‰. Rare Earth Element fractionation is visible in the most isotopically altered samples, which points to mobilization of these elements. The site of re-deposition of the leached elements may well be found in distal hydrothermal veins, which contain albite, calcite, apatite and REE-fluorocarbonates. The Matongo carbonatite thus appears as a complete metallogenic hydrothermal system where both the source and sinks of REE are identified.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Hadean crustal relics and evidence for lifetime of early crust

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The Nuvvuagittuq supracrustal belt (Québec) and the Acasta gneiss complex (NWT), Canada represent some of the oldest crustal remnants on Earth and are thus outstanding archives for inferring the early history of the continental crust. There are, however, controversies about how existing data should be interpreted in terms of geochronology and time scales. In this study, Sm-Nd isotope data, combined with U-Pb dating and Lu-Hf isotope data, were examined.

We analyzed thirteen samples, previously dated by U-Pb, zircon and Lu-Hf geochronology from the Acasta gneiss complex for high-precision $^{146,147}$Sm-$^{142,143}$Nd-systematics. The $^{147}$Sm-$^{143}$Nd data yield an alignment corresponding to an age of 3371 Ma age. Ten out of the thirteen samples show negative $^{142}$Nd anomalies with an average deficit of $-9.6±5$ ppm.

We show that, unlike previous claims, the $^{146}$Sm-$^{142}$Nd systematics are susceptible to resetting. Furthermore, when combined with the corresponding $^{146}$Sm-$^{144}$Nd and $^{176}$Lu-$^{176}$Hf data for the same samples, these data provide a fairly accurate picture of the evolution of Nuvvuagittuq and Acasta rocks. To examine quantitatively the effect of thermal resetting, we designed a new model whereby isotopes undergo exchange in a closed system at whole rock lengthscale. The Nuvvuagittuq mafic rocks were only partially reset, implying that direct dating of these rocks is not possible. In contrast, the degree of resetting was more extreme in Acasta, which yields rather constant $^{142}$Nd anomalies, while the $^{147}$Sm-$^{143}$Nd system records a younger age of $-3400$ Ma. In both cases, the existence of negative $^{142}$Nd anomalies can be attributed to Hadean crustal extraction between 4500 and 4300 Ma. The lifetime of this crust was investigated using time-dependent box models, including recycling into the mantle, and is shown to persist over 0.5-1 Gyr. In addition, the existence of positive $^{140}$Nd anomalies in younger rocks was found to depend strongly on this parameter, and on the mantle stirring time.

Diffusive heavy metal fluxes in bottom river sediments

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Suspended particles are scavengers of contaminants in streams. When they become deposited on the river bed they can act as efficient traps. Early diagenetic processes in bottom sediments are known to induce diffusive fluxes towards the overlying water in lakes and seas for some elements and downwards for others [e.g., 1, 2].

We applied to a river one of the methodologies commonly used for non turbulent water bodies, i.e., porewater *peepers*. The Lot River (in SW France) was selected because of its history of long-term metallic contamination and the consequent concern about the possible re-entering in the river dissolved flux of previously trapped heavy metals. The benthic pore water samplers (with a 10 mm vertical resolution) were installed manually by a SCUBA diver at a depth of ca. 2 m in a slow channel of the river.

The interstitial water redox potential, pH, dissolved sulfate and phosphate all decrease with depth, contrary to Fe and Mn which increase with depth. All of this is coherent with diagensis.

For Cd and Zn we observe a peak in dissolved concentration 1 to 3 cm below the sediment-water interface, this implies a double flux, one towards the river and the other towards the sediments. This last component is in favor of removal of Cd and Zn from the river flux to the ocean, but in turns it might cause some concern for groundwater supply in local well fields in alluvial aquifers. These observations are explained in terms of geochemical processes.

Particulate matter in São Paulo City: comparison between industrial and urban area

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Airborne particulate matter in urban atmosphere is derived from natural and anthropic sources. The chemical composition of coarse and fine particles is critical when considering their hazardous effect. This particulate matter study is part of a greatest research project that investigates the relationship between aerosols, road dusts and surface soils.

The sampling sites are located in two region (eastern and western zones) of the São Paulo City, in the two Campi of the University of São Paulo that present distinct characteristics i.e. industrial and commercial/residential backgrounds. The eastern area (EACH) is located in the floodplain of the Tietê River, near several industries, a highway and the international airport. The western area (Butantã) is located in a commercial and residential area and submitted to intense vehicular traffic.

The particulate matter (PM_{2.5} and PM_{2.5-10}) was continuously collected during day and night periods, simultaneously in the two areas. Sampling was initiated on August 22th, 2012 and finalized on December 7th, 2012 in the eastern area and from July, 7th to September 9th, 2012 in the western area. This period includes winter and the beginning of summer (raining season). Black Carbon and multi-elemental composition where quantified in the fine fraction by reflectometry and FRX, respectively.

The results show that particulate matter concentrations during winter, in the eastern area were 23.70 ±13.05 µg m⁻³ in the fine fraction and 42.73 ±37.71 in the coarse one. Concentrations in the western area were 21.09 ±14.00 µg m⁻³ in the fine fraction and 16.19 ±8.17 µg m⁻³ in the coarse one. During summer, concentrations were lower and similar between the two fractions. Concentrations were 20.05 ±7.72 µg m⁻³ and 17.75 ±13.93 µg m⁻³ in the fine and coarse fraction, respectively, in the eastern area. In the western area, concentrations were 17.25 ±8.36 µg m⁻³ and 17.09 ±8.12 µg m⁻³, in fine and coarse fraction, respectively. During winter, higher concentrations in the coarse mode in the industrial area may be due to higher soil resuspension since the vegetation area is reduced comparing with the western one. Chemical analysis are still being done but preliminary results showed that for the industrial area, black carbon contributed to 18.2% of the fine particulate matter mass. The elements with higher concentrations were S, Si, Fe, K, Al, Na, Zn, Pb and Cd.

New method for precise Cl isotopes measurement by SIMS

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Chlorine is an important volatile element. Its two stable isotopes are used to track the global halogen cycle and to determine fluid sources. Chlorine isotopes are fractionated by fluid/rock interaction, degassing, diffusion and mineralogical transformation. However, the range of Cl isotopes on Earth may be relatively limited [e.g., 1], requiring precise measurements of Δ³⁷Cl. Usually Cl isotopes are measured by TIMS or IRMS, and only a few measurements have been performed so far by ion probe. Previous SIMS studies reported a reproducibility of 0.8 to 1.5‰ (2 Standard Deviation (SD)) for glasses with > 200 ppm Cl [e.g., 1, 2]. We develop a new SIMS method to improve the precision of Δ³⁷Cl measurements. Analyses were done on a CAMECA IMS 1280-HR, using a cesium source. One analysis consists of two minutes presputtering using a 25µm raster to clean the surface, followed by 7 minutes of analysis using a ~10µm rastered beam. Δ³⁷Cl and Δ³⁵Cl were simultaneously measured on electron multipliers in multicollection mode.

Results show internal precisions as good as <0.2‰ (2SE) and reproducibility (spot to spot) of 0.6 to 0.8‰ (2SD) for standard glass with Cl content down to 100 ppm. For standard glasses with Cl content < 100 ppm (down to 5 ppm), the reproducibility reaches 1.5‰ (2SD).

With this precision reached it is now possible to investigate in situ Δ³⁷Cl variations at small scale, even in minerals with low Cl content, using the appropriate standard material.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Lu-Hf and Sm-Nd systematics of the first solids in the Solar System

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Hafnium-176 excesses are found in bulk chondrite and eucrite isochrons, and in some (not all) eucrite [1] and angrite mineral isochrons [2,3]. It was proposed that cosmic rays accelerated by supernova(e) shocks in the early Solar System could produce a higher decay rate of a 176Lu isomer within the irradiated planetary materials [2]. This hypothesis complicates the direct determination of the initial Lu-Hf isotopic composition of the Solar System and by extent that of the terrestrial planets [4]. The interpretation of the earliest terrestrial Lu-Hf isotopic records relies on knowing these initial conditions [5].

Such external irradiation sources should affect any objects already formed and exposed in the protoplanetary disk. We thus investigated the stable and radiogenic Lu-Hf and Sm-Nd compositions of CAIs, the first solids formed in the Solar System. The selected five CAIs were formed after injection of 26Al into the protoplanetary disk [6]. The 144Sm/152Sm ratios have the largest variations with p-process deficits typically at ~250ppm. Deficits in 149Sm (~100ppm) are correlated to excesses in 150Sm within the same CAI suggesting small neutron capture effects. All stable Nd isotope ratios have deficits smaller than 50ppm. The bulk CAIs have no resolvable Hf isotopic variations for 174Hf, small positive anomalies (<20 ppm) for 178Hf and 180Hf which demonstrate minimal corrections (<40ppm) for 176Hf/177Hf ratios. The bulk and mineral 147Sm-143Nd and 176Lu-176Hf isochron ages for three melted CAIs together are 4519 ±140 Ma (MSWD = 0.77, 143Nd/144Nd= 0.50675 ±20) and 4560 ±190 Ma (MSWD = 59, 176Hf/177Hf = 0.27985 ±15) respectively. We thus interpret the anomalous Lu-Hf isochron slopes [1,2] as the consequence of secondary parent body processes. Our direct determination of the initial 176Hf/177Hf of the Solar System is consistent with, but less precise than, those obtained from present CHUR values and from updated bulk chondrite isochrons [7].


Ion concentration at the kaolinite – water interface

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Kaolinite is a clay present in soils, sediments and rocks, including sandstones and carbonates, as well as shales and mudstones. Its high surface area and large cation exchange capacity make it reactive in natural environments. For example, it plays an important role in uptake of contaminants in the environment and in tertiary oil recovery.

To observe the surface chemical composition of kaolinite, as it is during contact with solution, we used X-ray photoelectron spectroscopy (XPS) with the fast freezing technique. This allows the mineral - fluid interface to be preserved and investigated, even under ultrahigh vacuum which is necessary for XPS, because the ion distribution is “frozen in” as it was in the original liquid phase.

Solutions investigated were NaCl, CaCl2 and Ca(C2H5COOH)2 at pH 5.5, in their reaction with pure kaolinite (KGa1-b). The results show that the relative ion concentration is different at the surface than in the bulk, consistent with electrical double layer (EDL) theory. We also observed that the ratio of Ca and Cl ions is not constant with distance out from the interface. For low CaCl2 concentrations (< 6 mM), the Ca:Cl ratio is higher at the interface, whereas at higher Ca concentration, more negative counter ions, i.e. Cl, are present to balance charge. Results from molecular dynamics (MD) simulations (figure) and atomic force microscopy (AFM) experiments complement the XPS results with structural information to build a full picture of interface interaction.

MD simulation snapshot of Ca (orange) and Cl (green) adsorbed on kaolinite during exposure to solution. Water is present but we have made it invisible.
The co-evolution of Fe-, Ti-oxides and other microbially induced mineral precipitates during the diagenesis of sandy sediments

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Ilmenite (FeTiO₃) and related Fe-, Ti-oxides are ubiquitous components of modern beach sands and are often associated with “fossil” microstructures in ancient sedimentary rocks [1,2]. The mineral composition of the ancient sedimentary rocks we see today, however, differs from what was originally formed in the sediments billions of years ago. This change in composition is usually attributed to long, complicated histories and atmospheric influences, while the contribution of microbes is not typically considered. Here the goal is to understand the co-evolutionary path of microbes and minerals in sandy, shallow sub-aquatic environments under early diagenetic conditions. Laboratory experiments were done to document the precipitation of minerals on cyanobacterial cellular material as well as the phase changes in natural ilmenites to determine if microbes passively influence mineral phase pathways. The precipitates, ilmenite grains, and fossilized cells were analyzed using scanning electron microscopy (SEM), x-ray diffraction (XRD), and micro Raman spectroscopy. The results show that microbial fossilization occurs and a variety of mineral phases precipitate under early diagenetic conditions (T<70°C) in wet, sandy environments. The minerals that form in the presence of microbes differ in crystal habit and chemical composition from those without microbes. This study aids in understanding the microbial role in diagenesis and helps redefine geochemical biosignatures that can be used for the detection of ancient microbial life in sedimentary rocks on Earth as well as for future planetary life exploration missions.


Using Genomics to Reveal the Secrets Underlying the Ecological Success of Marine Diatoms

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Diatoms are thought to be the most successful group of eukaryotic phytoplankton in the modern ocean. Recently completed whole genome sequences from two species, Thalassiosira pseudonana and Phaeodactylum tricornutum, have revealed a wealth of information about the evolutionary origins and metabolic adaptations that may have led to their ecological success. A major finding is that they have acquired genes both from their endosymbiotic ancestors and by horizontal gene transfer from marine bacteria. This unique melting pot of genes encodes novel capacities for metabolic management, for example allowing the integration of a urea cycle into a photosynthetic cell. Our studies focus on P. tricornutum and exploit the availability of techniques for reverse genetics, digital gene expression profiling, genome and epigenome maps, ecotypes with differential capacities to adapt to different conditions, and distinct morphotypes that can be induced to change shape in response to ecologically relevant stimuli. Using these resources we explore both the physiological functions of diatom gene products and the evolutionary mechanisms that have led to diatom success in contemporary oceans.

A next objective is to explore the functional roles of diatom biodiversity in the world’s oceans. With biology becoming quantitative, systems level studies can now be performed at spatial scales ranging from molecules to ecosystems. Biological data generated consistently across scales can be integrated with physico-chemical contextual data for a truly holistic approach. While the marine planktonic ecosystems that diatoms inhabit comprise the base of the ocean food web, and are crucial in the regulation of Earth’s biogeochemical cycles and climate, their organization, evolution and dynamics remain poorly understood. The Tara Oceans expedition was launched in September 2009 for a 3-year study of the global ocean ecosystem aboard the schooner Tara. A unique sampling programme encompassing optical and genomic methods to describe viruses, bacteria, archaea, protists and metazoans in their physico-chemical environment has been implemented. The project aims to generate systematic, open access datasets usable for probing the morphological and molecular makeup, diversity, evolution, ecology and global impacts of plankton on the Earth system, as well as to explore and exploit their biotechnological potential.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Global distribution of sulfate reduction rates in marine sediments

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Sulfate is the dominant terminal electron acceptor in marine sediments. Sulfate reduction proceeds under anoxic conditions and is supported by a variety of electron donors (e.g. hydrogen, acetate, methane, propane, and butane), most of which are supplied by the decomposition of sedimentary organic matter. Consequently, a combination of primary productivity and water column depth is often thought to control sulfate reduction throughout most of the ocean’s seafloor [1, 2]. However, global models of sulfate reduction do not resolve the many different physical and ecological parameters that are encountered on a global scale, and that ultimately play a major role in driving local and regional sulfate reduction rates. We sought to better determine sulfate reduction rates on a global scale, irrespective of region or location by 1) including sulfate profiles from diverse settings and 2) compiling multiple geochemical parameters that are relevant to sulfate reduction and can help discern the magnitude of sulfate reduction rates. All available sulfate concentration profiles from DSDP/ODP/IODP (to Exp. 312) and additionally those in the database Pangaea (www.pangaea.de) were compiled reaching a total >600 non-repetitive concentration profiles. Basic metadata describing the cores was included, such as water depth and distance to shore. Water column data such as minimum percent O2 saturation, bottom water O2, NO3-, PO43-, and concentrations of surface water chlorophyll a and POC [3, 4] were included as additional variables that describe the biogeochemical setting of the cores. All compiled data and concentration profiles were applied to a training algorithm to estimate global sulfate reduction rates. The result was the most precise depiction of global sulfate reduction rates at the highest resolution to date. Our model serves as a platform for the examination of biogeochemical processes on the global scale and lets us predict energetic constraints for microbial metabolism in the subsurface.


Geometry of carbon and oxygen isotope exchange fronts in the Alta aureole, Utah: Records of hydrodynamic dispersion and scale-dependent permeability during infiltration-driven metamorphism

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A carbon (C) isotope exchange front, periclase reaction front and an oxygen (O) isotope exchange front are developed with increasing distance from the igneous contact in dolomitic marbles of the south Alta aureole, Utah in response to infiltration-driven metamorphism of the marbles. Their relative distances from the igneous contact, approx. 100, 200 and 380 m, respectively, are consistent with down-temperature infiltration of water-rich fluid [X(CO2) <0.1 to 0.15] that was equilibrated isotopically with the adjacent Alta stock. At the aureole scale both the C and O isotope exchange fronts exhibit significant dispersion: there is significant variation in both δ18O and δ13C values at any given position for ≥50 to 100m to either side of the geometric centers of both fronts. Applications of one-dimensional models of advection-dispersion to these aureole-scale dispersed fronts yield a minimum dispersion coefficient of 2E-8 m2/sec. However at outcrop and bedding scale, steep, coherent gradients in both δ18O and δ13C exist at or near bedding boundaries between marble layers of contrasting lithology and isotopic compositions; modeling of these profiles requires much lower diffusion/dispersion coefficients in the range of 7E-12 to 1E-14 m2/sec.

The variable characteristics of the exchange fronts can be explained by scale-dependent heterogeneity and anisotropy in permeability of the marbles. Both C and O exchange fronts are characterized by significant dispersion at the aureole scale because of significant bed-to-bed variations in permeability, which are reflected by significant bed-to-bed variations in δ18O and δ13C values. These bedding-controlled variations in permeability lead to significant permeability anisotropy, with permeability parallel to bedding>>permeability normal to bedding. In contrast, permeability within individual beds appears to be relatively homogeneous, as suggested by relatively consistent mineral modes and homogeneous δ18O and δ13C values within individual beds, and by steep, highly coherent δ18O and δ13C gradients preserved at or near bedding boundaries.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Petrologic and Metasomatic Controls on H and Cl Abundances and Isotopes in Lunar Rocks

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Abundances and isotopic compositions of H and Cl have been measured in apatites from twelve lunar samples, permitting systematic comparison of relationships between these properties and other petrologic and geochemical characteristics. High d37Cl values are found in relatively H-rich apatites, apparently falsifying the hypothesis that elevated δ37Cl arises only from single-stage degassing of anhydrous magmas. Nevertheless, high δ37Cl is preferentially associated with relatively low H apatites and so seems to be a property of relatively degassed reservoir(s). The most H-rich apatites tend to have ‘low’ δ37Cl, < +25‰. Higher δ37Cl values (> +25‰) are seen only in highlands rocks and breccias, and the highest value is in a rock that may be from an impact melt/breccia sheet. Among the eight mare basalts analyzed by us and others, δD of apatite shows no correlation with H abundance or δ37Cl. δD is, however negatively correlated with pyroxene homogeneity [(minimum Mg#)/(maximum Mg#)]; basalts that experienced protracted thermal histories (igneous, impact, or metamorphic) have low δD. Finally, it is common to observe both significant heterogeneity in abundance and isotopic composition of H and Cl within apatite from a single sample, or even individual crystals, indicating a lack of equilibrium.

These results can be interpreted in terms of planet-scale evolution; for example, the high δ37Cl of highlands rocks could be inherited from a partially degassed (H-poor) magma ocean. However, it is also possible that elevated δ37Cl in some samples arose through devolatilization during impact metamorphism and/or metasomatism of the crust. Variations in δD could represent mixing of a high δD (> +500‰) component in pristine igneous rocks (either because this is a signature of their mantle sources or because of magmatic degassing) with a low-δD component like solar wind implanted into regolith. If so, much of the volatile element geochemistry of lunar rocks may reflect crustal and near-surface processes.

Hot spring environments as accessible portals into the metabolic underpinnings of the deep hot biosphere

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The Earth’s crust contains an extensive and diverse deep biosphere that is sustained by chemical energy under dark and oligotrophic conditions. Much remains unknown and in need of discovery in these ecosystems due to their deep and hard-to-reach nature. Herein, it is proposed that much information directly relevant to the deep, hot, biosphere of continental subsurface systems is directly accessible in the form of sediments and near-subsurface investigation in the globally relevant hot springs of Yellowstone National Park (YNP), Wyoming, USA. We investigated the composition of ~30 community metagenomes in YNP using a suite of bioinformatic and ecological modeling tools. The results suggest that the metabolic composition of microbial mat communities can be accurately predicted based on the physical and chemical attributes of the environment. Of particular significance is the strict temperature-dependent demarcation noted between the metabolic composition of chemotrophic communities and phototrophic communities as well as the pH-dependent demarcation in the metabolic composition of chemotrophic communities. Additional results from modeling and in situ activity-based studies will be presented that reveal the environmental constraints that shape the distribution of metabolic processes in these accessible portals to the deep hot biosphere.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Seasonal variation in biological methane production in a subglacial ecosystem

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Reports of seasonal plumes of methane emanating from the near sub-surface of Mars have fueled speculation that they may be the result of biological activity. The biological production of methane is catalyzed by a unique group of anaerobic archaea, the methanogens. Common to all methanogens is a unique metabolic pathway that enables methane production from a limited number of substrates such as H₂ + CO₂, formate, CO, methanol, methylamines, and acetate. Methanogens live close to the thermodynamic limit of life, a problem exacerbated at extremes of cold temperature. Here, we present genetic, physiological, geochemical, and thermodynamic data in support of the presence of a unique thermodynamic limit of life, a problem exacerbated at extremes of cold temperature. Here, we present genetic, physiological, geochemical, and thermodynamic data in support of the presence of a unique and active assemblage of methanogens in the near freezing (-0.1°C) and oligotrophic subglacial environment of Robertson Glacier, Alberta, Canada. Dominant methanogens present in the RG sediments may constitute a new order that bridges the physiologically distinct Methanomicrobiales and Methanosarcinales lineages. Methane flux measurements (2011) indicate seasonal variation in the release of methane from this permanently cold extraterrestrial analog environment.

What are the 146Sm-142Nd reference parameters for the Earth?

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Since the first publication of high precision 146Nd/144Nd ratios in chondrites [1], different early Earth differentiation models have been proposed. The excess in 146Nd measured in terrestrial samples relative to the average chondrite value requires that all terrestrial rocks sampled by volcanism over the Earth’s history come from a geochemical reservoir characterized by a super-chondritic Sm/Nd ratio. Some authors proposed that the complementary enriched reservoir has been lost during the Earth’s accretion [2,3] whereas others suggested that a hidden reservoir may have been preserved in the deep Earth [1,4]. The measurement of stable Sm and Nd isotope ratios in chondrites has created additional confusion in the interpretation of 142Nd deviation. Different groups of chondrites clearly have different 142Nd signatures and variations in stable Sm and Nd isotopes were found [5-7], all of which likely reflect different mixtures of r-, s-, and p-process nucleosynthetic products.

We will present a summary of the data available on Sm-Nd systematics of chondrites as well as new data obtained on enstatite chondrites (whole rocks and leaching experiments), achondrites and CAIs from CV3 chondrites. On the basis of these results, carbonaceous chondrites must be considered as a minor constituent of the Earth. Enstatite chondrites overlaps with the terrestrial 142Nd/144Nd ratio. CAIs Sm/Nd-142Nd/144Nd isochrons pass through the terrestrial value.

Considering the level of precision now achieved on Sm-Nd isotope measurements and looking at the results obtained on stables Sm and Nd isotopes our opinion is that the Earth-chondrite difference in 142Nd suggests that silicate part of Earth experienced a very early differentiation event. However these models will be discussed considering these new results.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
A bioturbation-induced decrease in atmospheric oxygen across the Precambrian-Cambrian boundary

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Bioturbation is the reworking of sediments by animal motility, and its emergence across the Precambrian-Cambrian boundary occurred against the backdrop of major changes in the biogeochemical cycles of oxygen, phosphorus and organic carbon. Bioturbation substantially increases sedimentary phosphate content, limiting the phosphate available for primary production and thus reducing the marine organic carbon burial flux, which is the source of atmospheric oxygen over geological timescales. We use simple modelling to show how an increase in marine organic phosphate burial associated with the onset of bioturbation caused a net decrease in atmospheric oxygen across the Precambrian-Cambrian boundary. The resulting deoxygenation of the ocean restricted the spread of oxygen-demanding bioturbating animals, and established negative feedback loops that stabilised atmospheric oxygen at a lower level. Although more data are needed to quantitatively constrain model parameters, our results are supported by evidence for a resurgence of anoxic and sometimes euxinic conditions in the early Paleozoic.


The rate of iron compounds precipitation from AMD waters in the Łękińica region (the Muskau Arch, western Poland)

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The Muskau Arch is a large horseshoe-shaped glaciotectonic belt formed mainly during the Mid Polish Glaciation. Lignite deposits containing pyrite were excavated there till the end of the 70-ties of the 20th century. Abandoned excavations are recently filled with water forming large so called “anthropogenic lake district” (with about 110 reservoirs). Oxidation of sulphide leads to the generation of abundant quantities of sulphuric acid. Therefore many of these lakes, especially at the Łękińica area, are of acidotrophic type characterized by low and very low pH values (usually < 4.0). This is associated with the formation of numerous ochreous precipitates as a consequence of iron oxidation and hydrolysis. The aim of this study is to assess the precipitation rate of iron compounds from acid mine drainage waters. Experiment was conducted in over one year period, from July 2009 to September 2010, in eleven locations. For this purpose, unglazed ceramic plates (dimensions: 10x10 cm) were, after removing possible traces of iron, placed on the bottom of selected lakes. The plates were collected monthly and the amount of precipitated iron compounds was evaluated by the determination of Fe leachable in hydrochloric acid. The precipitates were investigated via X-ray diffractometry and SEM-EDS. The amount of precipitated iron compounds turned out to be very variable, ranging from ca. 50 [mg Fe*cm⁻²] per month to nearly 13 000 [mg Fe*cm⁻²] per month. The average value for all monitored locations was approximately 1 100 [mg Fe*cm⁻²] per month. X-ray diffractometry indicate that the only mineral phase formed was schwertmannite – poorly crystalline iron oxyhydroxysulfate. Images obtained with use of scanning electron microscope reveal the presence of numerous bacteria structures, confirming that the precipitation of schwertmannite was microbially-mediated.

This work was supported by AGH-UST (Faculty of Geology, Geophysics and Environmental Protection statutory grant).

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
**Coupled LA U-Pb chronology of detrital zircon and rutile: A powerful provenance tracer**

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The development of improved precision dating methods, increased diversity of methods and proliferation of high spatial resolution approaches in recent years has made a dramatic impact to Earth Science research. However, focusing on the right method/procedure to address different geological problems is essential to solve problems and maximise the impact of research. Dating techniques are widely applied to provenance studies in order to discriminate between potential source areas, to track the evolution of river drainage basins, to assess sediment budgets and erosion patterns across orogens and to infer feedback relationships between erosion, tectonics and climate. These methods involve high throughput analysis, and it is not uncommon to lose sight of the complexity of zircon and other grains in relation to the problem being addressed.

We have developed a new approach to LA-ICP-MS U-Pb dating of rutile and characterised two new reference materials [1]. We have also refined an approach to LA ICP-MS U-Pb dating of detrital zircons that uses CL imaging to identify and date all zircon components with a focus on very thin (≤5 µm) rims that record the latest growth events that otherwise would be missed due to their <5 µm width on a polished surface.

U-Pb dates on zircon and rutile records medium- to high-temperature igneous and metamorphic crystallisation events and cooling through ~500 °C, respectively. The U-Pb analysis of detrital zircon and rutile from the same sample allows tracking of multiple crystallisation and tectono-thermal events of the source areas over a broad range of temperatures in a much more definitive and revealing manner than zircon alone. This is key to provenance studies where the detritus is sourced from areas with complex polyphase metamorphic histories such as collisional orogens. We have applied our method to Himalayan-derived sediments in the Eastern Himalaya to unravel Neogene tectonic-erosion relationships, and have found rutile and zircon rim ages as young as 1 and 5 Ma, respectively, inferring derivation from the Namche Barwa eastern syntaxis area.


**Insight on formation and evolution of cratonic mantle: Re-Os dating of single sulfides from Somerset mantle xenoliths (Rae Craton, Canada)**

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Cratonic mantle xenoliths provide an unique opportunity to study the formation and evolution of the Archean lithosphere. However, widespread metasomatic processes that cause profound textural and geochemical changes, make it difficult to determine the original melting age. Mantle xenoliths from Somerset Island (North Rae Craton) are characterized by a large range of whole-rock Re-depletion ages (T<sub>RD</sub>) ranging between 1.3 and 2.8 Ga [1]. Moreover, the oldest samples have low Pd/Ir ratio inherited from the original melting process, whereas younger samples are characterized by variable enrichments in Pd, Pt and Re suggesting extensive metasomatic overprint [1].

To better constrain the age distribution in the mantle root of the Rae Craton and to evaluate whether cratonic lithosphere formation may be older than recorded by the whole-rocks, we performed a Re-Os isotopic study on sulfides from four mantle peridotite xenoliths showing variable HSE (highly siderophile elements) signature (Pd/Ir=0.03-0.6). Sulfides (down to <10 µm) were micro-sampled from thick sections, with Os extracted via µ-distillation and analyzed by N-TIMS. Sulfides from the peridotite with the most HSE residual signature yield T<sub>RD</sub> ages of 2.7-2.8 Ga, in agreement with its whole rock T<sub>RD</sub> age. Sulfide T<sub>RD</sub> ages from metasomatised xenoliths vary from 2.8 Ga to future ages, with the 2.8 Ga age significantly older than the whole rock T<sub>RD</sub> ages (even T<sub>MA</sub>). The 2.7-2.8 Ga age, recorded in sulfides from three xenoliths out of four, overlaps with widespread magmatism in the Rae Craton [2] suggesting possibly a synchronous event of crustal and lithospheric mantle formation. Our results show that xenoliths with residual HSE signatures are likely to preserve the original melting age while the more metasomatic xenoliths have been rejuvenated by extensive addition of ‘younger’ sulfides.


DOI:10.1180/minmag.2013.077.5.2

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Ocean drilling: MORB geochemistry in the third (and fourth) dimension

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Most of our knowledge on the composition and formation of the oceanic igneous crust derives from lava samples collected from active ridge axes by dredging or submersible. However, lavas erupted at the ridge axis eventually make up the lowermost part of the extrusive section. If these differ in composition from those emplaced off-axis, then compilations of axial mid-ocean ridge basalt (MORB) may not yield an accurate estimate of the composition of the bulk crust.

Lavas drilled from the oceanic crust provide another way to estimate the composition of the bulk crust. In addition, they record changes in MORB chemistry over both long and short timescales. We have shown previously [1] that mantle temperatures recorded in the major element composition of ancient drilled MORB vary systematically over long timescales. The chemical stratigraphy of lavas from individual drill sites could be used to investigate chemical changes over $10^3$ to $10^5$ timescales, which may result from variations in fractionation, magma replenishment rates or source and melting effects.

We carried out major element analysis of 340 fresh glasses from 30 different DSDP and ODP sites in the Atlantic and Pacific. First results indicate that lavas from single drill sites are remarkably uniform in their chemical composition when compared to the chemical variation present at the corresponding segment of the active ridge axis. We find systematic chemical variations with depth, sigmoidally shaped in the fast-spread crust of site 1256D, drilled into superfast-spreading crust. This may indicate major differences in the residence time of magma in crustal magma chambers as well as in the magma replenishment rate, e.g. size and time intervals of rising magma batches. The oscillation between magmatic differentiation and magma recharge may be responsible for some of the globally observed trend element patterns in MORB as recently suggested by [2] but based on predominantly dredged samples.


Testing models for continental growth and melt-rock interaction from $^{186}$Os-$^{187}$Os isotopes in southwest usa mantle xenoliths

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Melting in the convecting mantle results in lower density residual peridotite that may stabilize as subcontinental lithospheric mantle (SCLM), results in juvenile crust production, and is likely a primary mechanism to grow continents over Earth history. Peridotite and pyroxenite xenoliths provide a compositional record of formation and subsequent modification of the SCLM.

Xenolith samples 3 classic locales in the Southwestern United States - Dish Hill (California), Kilbourne Hole (New Mexico), and Vulcan’s Throne (Arizona), span an 860 kilometer-wide region within two crustal provinces, the 2.0-2.3 Ga Mojavia, and the 1.7-2.0 Ga Yavapai-Mazatzal provinces. Preliminary $^{186}$Os-$^{187}$Os data for spinel-bearing peridotites show positive correlations with melt depletion indicators such as $\text{Al}_2\text{O}_3$. Applying the aluminachron age concept gives $^{187}$Re-$^{187}$Os model ages ranging from 2.0 to 2.3 Ga, broadly consistent with the ages of the overlying continental crustal provinces. If so, these data suggest models where continental growth is directly linked to stabilization of its underlying SCLM via partial melting in the convecting mantle. It also indicates that large off-craton continental regions may grow in rapid pulses through large-scale mantle melting events. A potentially viable alternative is that the aluminachrons record melt-rock interaction subsequent to earlier partial melting. If so, then these data instead only provide minimum model ages of partial melting via the lowest $^{187}$Os/$^{188}$Os ratio measured in each suite and thus may be unrelated to the initial stages of juvenile crust production leading to continental growth, and alternatively represent later continental magmatic processes.

To further evaluate the timing and mechanisms of SCLM stabilization and evolution and their potential link to continental growth, Os isotope data for pyroxenites from these locales will be presented to constrain compositional signatures imparted to the peridotites via melt addition or melt-rock interaction. Further, the first high-precision $^{186}$Os-$^{187}$Os measurements of continental peridotite xenoliths will be obtained to monitor Pr-Re-Os fractionation events. Coupled $^{186}$Os-$^{187}$Os fingerprints partial melting versus melt-rock interaction to the Os budgets of each of these xenolith suites.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Solid solution formation and uptake of Radium in the presence of barite

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The phase relations in the BaSO4-RaSO4-H2O system may determine the solubility of radium in natural waters due to the formation of a solid solution. In the near-field of nuclear waste repositories for spent fuel, radium may enter a system in which barite is in equilibrium with the aqueous solution. Thermodynamically, a RaxBa1-xSO4 solid solution is expected to form as solubility controlling phase rather than RaSO4. However, due to a lack of reliable data, the solid solution system RaSO4-BaSO4-H2O is currently not considered in long term safety assessments for nuclear waste repositories. The solubility product of the pure RaSO4 endmember is poorly constrained between pK RaSO4 = 10.26 to 10.41 by only very few experimental data [1,2]. Published interaction parameters W BaRa of the RaSO4-BaSO4-H2O system varies varies in different studies [3, 4] between 0.9 and 3.9 - 6.5 kJ/mol.

In this study we have combined experimental data, atomistic calculations and thermodynamic modeling to study in detail how a radium containing solution will equilibrate with solid BaSO4 under repository relevant conditions. Batch sorption experiments at close to equilibrium conditions indicate the formation of a RaxBa1-xSO4 solid. Our first principles calculations based on the single defect method [5] indicate a value of W BaRa ≈ 2.5 ± 1.0 kJ/mol, implying a non-ideal solid solution. Thermodynamic assessment calculations indicate that the final experimental Ra (aq) concentration at room temperature and 90 °C can be matched with W BaRa ≈ 1.5 kJ/mol and pK RaSO4 ≈ 10.41.


The co-ordination of Boron in foraminiferal calcite

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The analysis of boron in foraminiferal calcite is a burgeoning palaeo-proxy for past ocean-acidification events [1]. This is particularly relevant to today’s ‘carbonated ocean’ [2]. However, considerable uncertainty surrounds the mechanisms of boron incorporation into the shell. Foraminiferal calcite is known to be highly chemically heterogeneous [3], and understanding how boron fits into this complex structure is central to our understanding of, and confidence in, this important proxy.

We have applied synchrotron NEXAFS spectroscopy to examine the distribution and coordination of boron in foraminifera at the nm length scale.

Figure 1: A Scanning Transmission X-ray Microscope (STXM) image of a section of foraminifera test at the trigonal B edge, showing variations in the concentration of B [4].

STXM results reveal clear homogeneity in boron concentration, which appears to be uniformly hosted in a trigonal coordination in the calcite crystal lattice (BO3 groups). Analysis of boron coordination is ongoing.

The establishment of the steady-state activity at Stromboli volcano (Italy): evidence from diffusion and mixing processes revealed at mineral scale

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The present-day activity of Stromboli is characterized by strombolian explosions ejecting black scoriaceous lapilli and ash. This persistent activity is interrupted by effusive eruptions and more energetic explosions (paroxysms) also emitting a small volume of light pumices. The entire system is in a persistent steady-state activity whose driving forces are still not completely understood. Investigating the evolution of the plumbing system toward the present-day condition is thus crucial to better constrain and understand the onset and development of the present-day activity.

We studied in detail two selected samples representative of the transitional eruptive period from the more explosive phase forming the Pizzo Sopra la Fossa tuff cone (ca. 2 ka) to the present-day activity: (i) an older spatter-lava sample (shoshonite) from the Post-Pizzo fountain-fed fallout activity; (ii) a large and flattened, black scoriaceous spatter (shoshonitic basalt) probably ejected during one of the early paroxysms of the present-day activity. Both samples have similar paragenesis with phenocrysts of olivine, clinopyroxene, plagioclase. We recognize several types of clinopyroxene textures with different recurrence among the two samples. In detail, multiple banded clinopyroxene with evident resorption features, characterizes the older sample, recording several pulsatory intrusions of new mafic magmas into the system and pointing to the establishment of the steady-state condition. Contrarily, single diffused band and/or patchy cores are found in the present-day sample. We applied the diffusion chronometry to suitable clinopyroxene crystal zones to estimate the timing of these refilling events in the shallow magma reservoir from the Post-Pizzo period onward pointing to a progressive transition toward the present-day steady-state conditions.

A δ13C record from marine carbonates deposited below diamictites between ca. 2430 and 2440 Ma

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Palaeoproterozoic Polisarka Sedimentary Formation diamictites underlain by marine carbonates and overlain by volcanic ash sediments were recovered from International Continental Scientific Drilling Program Fennoscandian Arctic Russia - Drilling Early Earth Project (ICDP FAR-DEEP) Hole 3A (Kola Peninsula, NW Russia). The tuff yielded 2434 Ma dated zircons, constraining deposition of the diamictites and underlying carbonates to within an interval ca. 2430 to 2440 Ma. The carbonate rocks originally included aragonitic limestones deposited mostly in a deep-water setting. They record two inorganic carbon δ13C excursions, from values of ca. 0‰ to minima of ca. -5.4‰ as the diamictite is approached. Mg/Ca ratios correlate strongly with δ13C in the sections containing the excursions. Combined with petrographic observations, this correlation reflects secondary alteration of the first excursion, and resedimented dolostone clasts in the second excursion. It is tempting to speculate that these dolostone clasts were deposited in penecontemporaneous shallow-marine waters as the global glaciation began. Their low δ13C values might reflect input of oxidised atmospheric methane to the ocean surface (and therefore the cause of the glaciation), while the majority of the ICDP FAR-DEEP Hole 3A carbonates record deeper-marine inorganic carbon δ13C.
Dolomite formation within microbial mats from the Dohat Faishakh sabkha, Qatar

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The hypersaline coastal sabkha of Dohat Faishakh (Qatar) was one of the first settings recognized as a rare modern geological environment where dolomite formation occurs (Illing et al., 1965). Although the origin of dolomite remains one of the most debated subjects in sedimentary geology, microbial mediation has been recently proposed as a possible solution for this controversy. Until now, the relationship between microbial activity and dolomite precipitation in the Dohat Faishakh sabkha has not been evaluated. The limited previous studies of the Dohat Faishakh sabkha considered dolomite formation to be the result of a penecontemporaneous replacement of authigenic aragonite. However, no conclusive evidence confirms this hypothesis. To evaluate whether a “microbial factor” is important in this classic evaporitic environment, we collected core samples along a transect from the lower intertidal to the supratidal zone of the sabkha. A preliminary investigation of the sampled sediments revealed a close association between buried microbial mats and dolomite. The exopolymeric substances constituting the microbial mats are recognized as an important component for dolomite nucleation. We, therefore, hypothesize that the main factor controlling the occurrence of dolomite within the sediments of the Dohat Faishakh sabka is the presence of an organic matrix (i.e., the buried microbial mats) and not a replacement process transforming primary aragonite into dolomite. Aragonite and dolomite likely precipitate nearly simultaneously from highly evaporated marine waters. The presence/absence of an organic matrix determines whether the carbonate minerals will have a dolomitic vs. an aragonitic composition. Applying a geomicrobiological approach to study mineral formation beneath the Dohat Faishakh sabka will provide new insights into evaporite mineral associations in the rock record, as well as into extraterrestrial environments, as evidenced by recent observations of evaporitic sediments on Mars.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org

A new aqueous phase protocol for the mechanism generator GECKO-A used for the CAPRAM mechanism extension

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The ubiquitous abundance of organic compounds in natural and anthropogenically influenced eco-systems has put these compounds into the focus of environmental research. To investigate the chemistry of organic compounds in the tropospheric multiphase system, explicit modelling can provide a useful tool.

However, the oxidation of large organic molecules (typically Cₙ) involves a huge number of intermediate compounds produced during the oxidation process. Furthermore, most of the needed experimental thermodynamic and kinetic data are unavailable in the literature. Therefore, the creation of explicit mechanisms relies on automated self-generating mechanism construction as achieved with GECKO-A (Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere) for the gas phase.

As the chemistry in deliquescent particles and cloud droplets can be important for the oxidation process, a protocol has been developed to describe the degradation of aliphatic organic compounds in the aqueous phase. This aqueous phase protocol has been implemented into GECKO-A and was used to advance the aqueous phase mechanism CAPRAM 3.0n (Chemical Aqueous Phase RAlical Mechanism). The latest CAPRAM version was extended by about 3500 reactions, where, besides the addition of new subsystems, branching ratios were introduced in the mechanism.

Box model studies were performed with a non-permanent cloud scenario to reveal more insights into the degradation and formation of organic compounds in deliquescent particles and cloud droplets as well as the feedback on gas phase concentrations. Detailed time-resolved investigations of the chemical fluxes assisted the investigations of concentration-time profiles. Comparisons with previous model studies and experimental data from field and laboratory investigations were used to validate the mechanism generator and show significant improvements in the generated model results.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
**Rhenium-Osmium Isotope Geochronology of the Neoproterozoic Fifteenmile Group, Coal Creek Inlier, Yukon, Canada**

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New $^{187}\text{Re}^{187}\text{Os}$ isotope data on organic rich mudrocks from the Neoproterozoic Fifteenmile Group, Coal Creek Inlier, Yukon, Canada provide direct age control for biomineralizing scale microfossils [1] and the termination of the Bitter Springs isotopic stage in northwest Canada. The uppermost Reefal Assemblage of the Fifteenmile Group has a preliminary $^{187}\text{Re}^{187}\text{Os}$ isochron age of 752 ±44 Ma (2o; Model-3; MSWD 4.2; $^{187}\text{Os}/^{188}\text{Os}$ 0.42 ±0.22). The obtained age is identical within error to $^{187}\text{Re}^{187}\text{Os}$ ages from the correlated Wynniatt Formation, Victoria Island, Canada [2]. This result is also in good agreement with known $\text{U-Pb}$ TIMS zircon analysis which brackets the sampled portion of the Upper Fifteenmile Group between 811.0 and 717.4 Ma [3]. If the ~750 Ma age model is correct, the Bitter Springs isotopic stage could be younger or extend longer than previously thought (~800 Ma). A younger age for the Bitter Springs Stage may also impact global paleogeographical reconstructions based on anomalous global paleomagnetic records from the Bitter Springs stage [4]. These measurements also represent an important benchmark for the $^{187}\text{Os}/^{188}\text{Os}$ composition of Neoproterozoic seawater. The $^{187}\text{Os}/^{188}\text{Os}$ record is an emerging seawater proxy which has the ability to trace rapid climatic perturbations [5]. This proxy record can provide independent confirmation of climatic fluctuations observed in important Neoproterozoic $^{87}\text{Sr}/^{86}\text{Sr}$, $^8\text{C}$ reference sections [6]. Further $^{187}\text{Re}^{187}\text{Os}$ work on samples from the Fifteenmile Group is ongoing.


**How bugs get their food: Linking mineral surface chemistry to nutrient availability**

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The bio-acquisition of mineral-bound key nutrients by microorganisms is currently of great interest because of our desire to understand soil nutrient cycling. It has been shown that fungi seek out nutrient sources through expansive mycorrhizal networks, acting as biosensors for ‘tasty snacks’. The mechanism by which fungi extract nutrients from minerals is by combining bio-mechanical forcing of the structure [1] with subsequent chemical alteration [2]. Usually, release of nutrients from minerals is discussed in terms of bulk chemical content. Here, we present data showing the importance of the surface composition of biotite, a key terrestrial source of primary nutrients (in particular potassium), to influence nutrient availability. This gives us new insights into the mechanisms by which microorganisms weather minerals, aiding in soil formation.

A suite of batch potentiometric and electrophoretic titrations (pH 1-12 and 25 °C), were carried out to determine the surface chemistry and reactivity of biotite by quantifying protons consumed and metals released. Potassium was found to be preferentially removed from the biotite surface down to an average depth of ~ 20 nm at all pH values. A slight pH dependency of this removal and the proton consumption profile suggest a significant portion of K was removed from the structure immediately upon contact between the biotite surface and the fluid. The existence of such a K depleted surface suggests that microorganisms are required to physically break the mineral structure to access nutrients from newly created surfaces. Our data set underpins the need for an initial bio-mechanical forcing of the mineral surface prior to its chemical alteration, leading to increased weathering.

Biogeography of serpentinite-hosted ecosystems

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Ultramafic rocks in the Earth’s mantle represent a tremendous reservoir of carbon and reducing power. Upon tectonic uplift and exposure to fluid flow, serpentinization of these materials generates copious energy, sustains abiogenic synthesis of organic molecules, and releases hydrogen gas (H₂). To date, however, the “serpentinite microbiome” is poorly constrained: almost nothing is known about the microbial diversity endemic to rocks actively undergoing serpentinization.

We have obtained metagenomic and 16S rRNA tag sequence datasets from fluids and rocks collected in serpentinizing ophiolites in California, Canada, and Italy. The samples include wells which directly access subsurface aquifers, rocks obtained from drill cores into serpentinites, and natural, high-pH serpentinite springs that are presumably representative of deeper environments within the ophiolite complex. Our results point to potentially H₂-utilizing Betaproteobacteria thriving in shallow, oxic-anoxic transition zones and anaerobic Clostridia thriving in anoxic, deep subsurface habitats. Similar bacterial taxa and genes encoding hydrogenase enzymes were also observed in seafloor Lost City hydrothermal chimneys, indicating that we are beginning to identify a core serpentinite microbial community that spans marine and continental settings.

These data represent a unique opportunity to examine biogeographic patterns among a specialized set of organisms and genes and to explore their evolution during the uplift and obduction of mantle rocks onto continents over geological time scales. We are currently testing for correlations between these metagenomic data and the geochemical conditions and the geological histories of the host rocks with an ultimate goal of inferring an integrated metagenomic-biogeochemical natural history of the serpentinite habitats.

Characterization of natural gem diamonds and UV light sources using fluorescence spectroscopy

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Gemologists have used fluorescence reactions to long wave ultraviolet light for identification of gemstones for decades. Simple visible observations of fluorescence color, intensity, pattern, and duration have proven invaluable for separating natural diamonds and other gemstones from synthetic or treated equivalents. Fluorescence viewing and imaging, however, can only provide a limited amount of information about the lattice defects that produce the luminescence. Spectroscopy provides details about the nature of the fluorescence, the combinations of defects that produce the observed colors, and the effects of different excitation sources. Spectra collected from natural gem diamonds show blue fluorescence from N3 defects (415 nm), green from H3 (503.2 nm) and H4 (496 nm), orange/red from N-V centers (575, 637 nm), and yellow from a combination of several defects associated with a visible absorption band at 480 nm. Using variable excitation, three dimensional maps (excitation, emission, fluorescence) of the luminescence spectra from each defect reveal complexities that cannot be discerned visually. In addition to this fundamental fluorescence information, spectroscopy also allows characterization of the excitation light source output and evaluation of how it affects the fluorescence produced from a diamond. A wide range of UV light sources are currently used in the gem and mineral industry with large differences in output intensity and wavelength. Small variations in bulb/LED and filter materials can significantly impact the visual fluorescence, leading to inconsistent results. The use of fluorescence spectroscopy provides additional detail that is not available from visual observation to help to identify subtle differences produced by variable light sources as well as many of today’s modern gemstone treatments.
Hydrochemical patterns in a structurally controlled geothermal system

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In this study, we investigate a magmatic structurally controlled geothermal reservoir in North Sulawesi-Indonesia focusing on structural geology and hydrochemistry. A combination of a thermal-hydraulic model with hydrochemical modelling is the goal of this study. The running geothermal system is located above a subduction zone surrounded by a complex network of faults and repetitive volcanic eruptions.

Analyses of the samples collected from wells, hot springs, rivers and lakes show typically two types of water. Acid high saline waters were found in the northern reservoir area (pH: 2.7-3.2, electrical conductivity: 4620-9700 µS/cm). A similar water type rises above this reservoir through several hot springs (pH: 1.8-2.7) and a lake (pH: 2.5) located above the reservoir. A second type of reservoir water was observed in the South where wells show a pH range of 4.2 to 6.5 and conductivities from 400 to 1729 µS/cm. Neutral hot springs occur in the surrounding area with pH values ranging of 5.8 to 7.0. While the northern and southern reservoirs are only 2km away from each other we observe strong difference variability (redox conditions prevaling during the different ore deposits. The present study focuses on the Azegour skarn (Morocco). Located in the High-Atlas, the Azegour site is one of the rare Mo-W-Cu exploited skarns (three historic mines). It is formed by a granitic intrusion (271±3Ma) in cambrian volcano-sedimentary serie composed by schists, volcanic complex (andesites, pyroclastites) and carbonate formations (calcareous and dolomites). The skarn takes place in the carbonate formations where pyroxenites and granitites occurred. The granitites being the Mo-bearing minerals in the form of molybdenites.

Molybdenite sampling has been performed in the main mine (Azegour) and in the Tizgui mine (1km north of the Azegour mine). The Mo isotopic composition has been determined on molybdenites using a MC-ICP-MS Neptune after aquaregia dissolution and adjustment to [Mo] = 1µg.g⁻¹. The δ⁹⁷/⁹⁵Mo ratios have been normalized to NBS3134 and a reproducibility of 0.07‰ (2σ) is reached.

Presently, we have analysed 12 molybdenites from Azegour and 2 from Tizgui and 14 others are in progress. Regarding the first 14 samples, the δ⁹⁷/⁹⁵Mo samples vary between -0.40 and 0.32‰ for Azegour and between 0.08 and 0.30‰ for Tizgui. It is worth noting that variations can occur either at the whole site (difference of about 0.72‰) but also at the cm scale in the same sample (here the largest observed difference is up to 0.40‰).

Regarding the Azegour skarn, there is no direct relationship for explaining the Mo fractionation in molybdenites between the facies or the two sites of sampling. Different processes will be discussed to explain the observed variability (redox conditions prevailing during the molybdenites deposits, late metamophism phase...). Further investigations using Pb and S isotopic compositions will help deciphering the oxidation state and the origin of molybdenites regarding the possible different fluids.

DOI:10.1118/minmag.2013.077.5.2
www.minersoc.org
Experimental constraints on HSE fractionation during basalt genesis

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Terrestrial basalts are characterised by CI-normalised depletions in the highly siderophile elements (HSE), as well as moderate to large interelement fractionation within the group; the IPGE (Os, Ir, Ru) are relatively depleted compared to the PPGE (Rh, Pt, Pd), Au and Re. The overall low abundance of the HSE in basalts is attributed to core formation, whereas the origin of the fractionation within the HSE group has been less certain. Experiments and empirical observations indicate that Ir, Ru and Rh are compatible in olivine, as is Ru in ferric-iron-poor chromian spinel, and both phases strongly reject Pt, Pd, Re and Au. It is expected, but unproven, that cpx and opx will exhibit broadly similar partitioning behaviour as olivine. This sense of fractionation is correct for terrestrial basalts, but the magnitude of partition coefficients is too low to account for the overall depletion levels.

Residual sulfide, either as liquid or crystalline MSS, has a significant impact on basalt HSE levels, owing to large sulfide-silicate partition coefficients. Crystalline MSS can be stable with silicate melt if the silicate liquidus is suppressed by water. Based on known MSS-sulfide melt partitioning, MSS-silicate melt partitioning can impose a strong inter-HSE fractionation, whose sense and magnitude is similar to terrestrial basalts. With the exception of Au, however, direct measurements of MSS-sulfide melt partitioning of the HSE have not been done. If melting occurs at higher temperatures, MSS is replaced by sulfide liquid. Experiments show that Re and Au are significantly less compatible than PGE in sulfide liquid at moderately oxidised conditions, accounting for the relative enrichment of Re and Au in terrestrial basalts. It is not clear, however, if sulfide liquid can impose IPGE/PPGE fractionation on silicate melt, as partition coefficients for these elements are currently too imprecise.

Recent measurements indicate sulfide-silicate partition coefficients for the PGE are on the order of 10^6 or larger. Since the mass fraction of sulfide liquid decreases during melting, this implies that the PGE content of residual sulfide could reach 1000s of ppm, leading to saturation in the less soluble PGE, such as Os, likely alloyed with Ir and Ru. The HSE content of terrestrial basalts might therefore be controlled by a combination of metal solubility and sulfide-silicate partitioning. Detailed modelling of this behaviour is considered by Mungall [this session].

Evidence for supernova injection into the solar nebula and the decoupling of r-process nucleosynthesis

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Variations in the non-radiogenic isotope abundances of meteoritic materials have long been interpreted as nucleosynthetic signatures resulting from the input of distinct materials produced from p-, s-, and r-processes [e.g., 1-8]. Previous studies of the Solar System’s first solids, calcium-aluminum-rich inclusions (CAIs), have demonstrated that isotopic compositions of various elements differ from terrestrial compositions and may be modeled using addition or subtraction of different nucleosynthetic components [6-8]. However, these studies did not determine the isotopic compositions of multiple elements spanning a large mass range in the same CAIs. We present for the first time an integrated study of Sr, Mo, Ba, Nd, and Sm isotopic compositions determined on multiple coarse- and fine-grained CAIs from the Allende CV3 chondrite.

The data demonstrate that the isotopic compositions of these elements in CAIs are uniform and yet distinct from the average Solar System, necessitating that CAIs were formed in a homogenous and isotopically distinct reservoir. Taken in whole, the observed mass-independent anomalies cannot be explained by: (1) presence of presolar components, (2) simple addition/subtraction of r-process nuclides, (3) incomplete digestion of the sample, (4) nuclear field shift fractionation, or (5) neutron capture. Relative to terrestrial standards, CAIs contain positive r-process anomalies in isotopes A<140 and negative r-process anomalies in isotopes A>140. Previous work has suggested that multiple supernova sources are required to account for the proportions of short-lived isotopes in the early Solar System [9]. The fundamental difference in the isotopic character of CAIs around mass 140 is consistent with [9] and necessitates (1) the existence of multiple sources for r-process nucleosynthesis, and (2) the injection of supernova material into a reservoir untapped by CAIs.

Noble gases as physiological tracers for gas dynamics in human blood

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The exchange of the inert noble gases (He, Ne, Ar, Kr, Xe) between gas and liquids is controlled solely by the gas-exchange kinetics in the gas/liquid interface, and by the solubility equilibrium (Henry’s Law). Noble gases are therefore excellent tracers for the physical processes involved in gas/fluid exchange, and they have widely been applied as environmental tracers in aquatic systems. Here, we present our first attempts in using noble gases to trace physiological processes in the human body, such as the gas exchange in the lung or the gas distribution within the human organism.

Blood samples were taken from an atecubital vein. Samples were transferred into copper tubes (sample containers) without exposure to air or any other gas phase, and copper tubes were sealed. After coagulation of the blood, the samples were centrifuged to separate the liquid blood plasma from the blood cells. Blood samples were then analysed by vacuum extraction and mass spectrometric quantification of the dissolved gases using the standard methods used for water and sediment samples.

While breathing ambient air, noble gas concentrations in blood plasma were very similar to those in air-saturated water. However, the $^{3}$He/$^{4}$He ratio was 10% higher in blood than in air-saturated water, which is possibly due to the difference in diffusivities of $^{3}$He and $^{4}$He isotopes in the air/blood interface of the lung. Also, the heavier noble gases were found to be enriched in the blood-cell fraction relative to the blood plasma.

Breathing air enriched with noble gases resulted in an increase of the noble gas concentrations in the blood, and a new steady state was attained within a few minutes. All noble gas concentrations increased with the same kinetics. This suggests that gas exchange is not limited by diffusion through the air/blood interface in the lung, and that solubility equilibrium is attained in the lung. In contrast to $^{16}$O₂, which is bound to hemoglobin, the steady-state noble gas concentrations were considerably lower than expected, which points to a secondary partitioning or loss of noble gases within the body.

Recent advances of noble gas geochemistry in aquatic systems

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Noble gases and biogeochemically conservative transient trace gases (SF₆, CFCs) in aquatic systems have commonly been used to determine water residence times and to reconstruct past environmental and climatic conditions.

Recent conceptual and experimental developments have considerably extended the applicability of noble gas and transient gas analysis in aquatic systems. The mechanistic understanding of the formation of excess air (EA), a surplus of dissolved atmospheric gases commonly observed in groundwater, now allows robust interpretation of EA as a proxy for the hydraulic conditions during groundwater recharge, e.g., in areas that were covered by ice sheets during the LGM. Recent experimental breakthroughs now allow noble gas analysis in sediment pore fluids and in fluid inclusions of speleothems to reconstruct environmental condition from minutes amounts of water. Furthermore, the coupling of vacuum systems commonly used for noble gas analysis with gas chromatographic methods allow combined analysis of noble gases and other gases (e.g., SF₆, CFCs, $^{18}$O, $^{15}$N) from a single water sample. This facilitates reliable EA correction for SF₆ and CFCs improving ground water dating. Finally, portable membrane-inlet mass spectrometers enable continuous and real-time analysis of noble gases and other dissolved gases directly in the field, allowing, for instance, quantification of $^{16}$O₂ turnover rates on small time scales.

In presenting these recent achievements, we intend to stimulate a broader discussion to define future applications of noble gases in conventional and unconventional aquatic systems.
How isotopic hydrogeochemical tools can help policy makers to target priority area for drinking water preservation?

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The main objective of the Water Framework Directive (2000/60/EC) is to prevent further deterioration, protect and enhance the status of aquatic ecosystems in Europe. In details, WFD enforces member states to identify the hydrosystems that should be protected for present or future use as drinking water. In this context, water policy makers of the Rhône-Méditerranée-Corse district (south-eastern part of France, covering 1/5 of the French territory) plan to list and delimit all the areas related to groundwater that present outstanding interests regarding quality and quantity for drinking use.

Our study is focused on two groundwater bodies located on the Rhône-Méditerranée-Corse district that have been identified as being of primary importance and/or at risk by the policy makers. These groundwater bodies (Isere alluvial aquifer and molasse aquifer) are used for drinking water supply for the large cities of Lyon, Grenoble and Albertville, to a lesser extent. Objectives were to characterize and better understand the origin of water and dissolved elements of these aquifers in order to identify the areas of major interest and protect them in priority. For that purpose, combined geochemical analysis of major and trace elements, and isotopes ($\delta^{18}$O, $\delta^{2}H$ of water, $\delta^{34}S$ of sulfates, $\delta^{87}$Sr/$\delta^{86}$Sr) have been successfully applied. This approach, in addition to geological and hydrogeological information, allow to identify groundwater units in each aquifer that i) present an uniqueness functioning and recharge and ii) permit low cost production for drinking purpose (water treatments reduced). For instance, the Isere alluvial aquifer presents high concentrations up to 3mg/L in As and Sb due to weathering of local rocks in the Alpes mountains. Hydrogeochemical knowledge, and especially isotopic tools, allow to target the groundwater units whose recharge area are less controlled by high As and Sb contents.

Lithium isotopic composition of the Tonga-Kermadec arc and its constraints on subduction recycling

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Understanding elemental transfer within subduction zones is integral to quantifying crust-mantle exchange and recycling. Lithium is water-soluble and potentially a useful tracer of subduction zone processes. We have analyzed the lithium concentrations and isotopic compositions of a suite of lavas from the Tonga-Kermadec island arc, as well as a depth profile through forearc marine sediments from ODP hole 204, and lavas from the Fonualei back-arc spreading center in order to trace how lithium isotopes manoeuvre through an intra-oceanic subduction zone.

The $\delta^{7}$Li of the entire suite of sediments and lavas vary from 0.3 to 14.4. The depth profile, along with published data from another nearby core sample (DSDP 595/596), shows a systematic increase in $\delta^{7}$Li (1.2 to 14.4) with depth. This is in relation with the sediment type: lithium isotopic signatures for pelagic sediments are often lighter because of fractionation from weathering, while volcanogenic sediments can be lighter or heavier as a direct result of their alteration effects. The $\delta^{7}$Li of hole 204 pelagic sediments overlap that of the mantle, but range to lower values (1.2 to 5.2), while the $\delta^{7}$Li of volcanogenic sediments are higher than the mantle (7.2 to 14.4). Thus, the Li isotope variation in the subducting sediments greatly exceeds that observed in the lavas. The fact that $\delta^{7}$Li in some arc lavas (0.3 – 7.6) falls outside the range of MORB requires enrichments by fluid transfer of lithium from the sediments (which is reinforced with published B/Be data). Lavas from the back-arc spreading center ($\delta^{7}$Li = 3.0 – 5.0) show no variation from the widely accepted lithium isotopic signature range of the MORB (1.5 – 5.5), suggesting that there is little Li transfer from the slab in the back-arc.

Electron flow in bacterial multi-heme cytochromes

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Understanding mechanisms and kinetics of electron transfer processes in environmental systems is an important frontier for molecular theory and computation. This presentation addresses elementary aspects of predicting electron transfer rates, demonstrates the essentiality of computational molecular simulation relative to lacking experimental probes, and establishes a new methodological state-of-the-art for this purpose, using bacterial multi-heme electron transfer proteins as the case study.

Electron transport to extracellular solid metal oxides by metal-reducing bacteria is a fundamental biogeochemical process optimized by evolution to catalytic perfection. To shed light into why and how individual electron transfer steps in associated multi-heme cytochromes are combined into overall molecular function, we carried out extensive computer simulations of the recently crystallized decaheme cytochrome MtrF. We report redox potentials of individual hemes, reorganization energies and electronic coupling matrix elements for heme-to-heme electron transfer in MtrF explicitly solvated in water. The free energy profile for electron flow along various evident heme ‘wire’ pathways was computed using thermodynamic integration and classical molecular dynamics, and could be related to differences in the charged amino acids local to specific hemes. Reorganization free energies yield a range consistent with theoretical expectations for partially solvent exposed cofactors, and reveal an activation energy range surmountable for electron flow. Quantum mechanical calculations of electronic coupling matrix elements show a clear correlation between couplings and endergonic steps of through-protein electron transfer, suggesting that the protein evolved to harbor low-potential hemes for thermodynamic range without slowing down electron flow.

Because the individual hemes are not easily distinguished spectroscopically in such proteins, none of these insights are experimentally accessible. The theory and simulation campaign on this system is thus not only enabling a fundamental advance in understanding bacterial electron transfer protein function and key design elements, but it also provides a window into the broader biogeochemical context by the evident selection pressure underlying its purpose.

Storage of Hadean oceanic crust in the Kaapvaal subcratonic mantle

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Eclogites from the subcratonic lithosphere appear to be ancient and Re-Os isotope data from eclogite xenoliths from Newlands on the Kaapvaal craton suggest that some may date back to the Hadean [1]. If mantle eclogites are products of subduction of oceanic crust [2], their ages place strong constraints on the beginning of plate tectonics. The calculated bulk rock compositions of a subset of bimineralic and of kyanite and corundum-bearing eclogite xenoliths from the Bellsbank diamond mine (about 30 km north of Newlands) have similar flat middle to heavy REE patterns. Their range and that of their calculated major element compositions lies within the range of modern day mid ocean ridge basalts and gabbroic rocks. The kyanite- or corundum-bearing eclogites (3 samples) display positive Eu anomalies and show depletion in the more incompatible trace elements except for an enrichment in U and Th. In accord with earlier work we interpret them as former plagioclase rich cumulates which were possibly slightly modified by dehydration during subduction and during metamorphism. We interpret the bimineralic eclogites with overall higher abundances of the more incompatible trace elements (2 samples; no Eu anomaly) as clinopyroxene-rich cumulates. Based on the chemical similarities we regard these eclogites as a co-genetic suite. The Lu-Hf two-point isochrones from these samples with temperatures of last equilibration above 920 °C give kimberlitic eruption age (≈ 120 Ma for Bellsbank), i.e. garnet and clinopyroxene were in continuous isotopic exchange in the mantle until the time of eruption. The reconstructed bulk rock Lu-Hf isotopic compositions of four of the five samples plot along a line in an isochron diagram which yields 4.12 ± 0.27 Ga (MSWD = 0.04) with tHf ~0. The reality of an Hadean age is supported by the extremely high tHf(t) values up to 1004 and 1006 respectively for coexisting cpx and garnet. Further support comes from garnet model ages between 3.13-3.5 Ga. These are minimum possible ages. Values of δ18O lower than the mantle (2.5‰ to 4.8‰ in garnets) are consistent with low temperature sea floor alteration as their cause. This supports the existence of oceans 4.1 Ga ago. The eclogites and their MORB-like compositions imply modern day potential mantle temperatures, at least locally, and subduction underneath microcontinents in the Hadean.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Zeolites as ion exchanger in harsh ultra-alkaline conditions

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Cement based waste disposal is among the more important options to provide safe storage of non-recyclable often highly toxic waste.[1] Despite all engineering efforts, potentially contaminated ultra-alkaline concrete derived pore waters (pH 12 – 14) will always remain associated with cement based waste disposal. To avoid contamination of the environment due to slow leaching of the metals from these waste forms, engineered barriers are built around the waste disposal sites in order to provide containment. Such engineered barriers, needed to increase the safety level of the waste disposal sites, always incorporate a sorption sink capable of reducing the concentration levels of the toxic metals below specified safety limits.

Zeolites typically crystallize in alkaline, Na/Si/Al rich aqueous conditions and exhibit cation exchange properties.[2, 3] Therefore this family of crystalline porous materials has a significant potential as sorption sink in engineered barriers optimized to function in ultra-alkaline concrete derived pore waters.

Cs+ sorption was evaluated as function of Cs+ concentration (10-11 up to 10-5 mole L-1) and time (up to 180 days). The sorption results obtained in ultra-alkaline concrete derived pore water were compared with data obtained in electrolyte solutions at pH 8 containing identical Na+, K+ and Ca2+ concentrations.

The isotherms demonstrated an unexpected increased Cs+ sorption in pH 13 solutions as compared to pH 8 solutions with similar cation content. Sorption results in ultra-alkaline concrete pore water as function of time indicate chabasite and clinoptilolite as two zeolite frameworks stable in these conditions. This confirms results obtained in zeolite formation/transformation studies that indicated a strong stabilizing effect of the alkali cations on specific zeolite frameworks. Binary sorption isotherms confirmed that the selectivity series and calculated selectivity coefficients expected for chabasite and clinoptilolite at trace concentrations (<10-4 M Cs+) are also valid in ultra-alkaline aqueous conditions.


Determination of sources and flowpaths of nitrate in a karstic watershed

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The Marseillon spring is a strategic resource for the drinking water supply of the Aquitaine region (SW of France). Fed by deep Cretaceous limestone aquifer and local infiltration (favored by karstic limestone outcrop), it is threatened by increasing nitrate concentrations (from 10 to 25 mg/L in 20 years).

Measurement of δ15N-NO3 and δ18O-NO3 coupled with δ11B allows a good discrimination between the multiple potential sources of nitrate in the area [1]. Additional microbiological markers (bacteriophages, bacterioïdales) can offer better precision over the origin of fecal contamination [2].

This work presents a dynamic approach based on these natural isotopic and microbiological tracers measured over samples of Marseillon’s groundwater and local surface waters collected from October 2010 to January 2013. Their evolutions within each compartment allow a better understanding of nitrate origin and flow paths in the studied watershed.

Modifications of Cu isotopic ratios in coastal sediments in relation to the increased use of copper based antifouling paints

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Cu is released in water by weathering processes and human activities. It is widely applied on vines and used as a biocide in antifouling paints. This study aimed to assess the potential of Cu stable isotopes to identify Cu sources in coastal sediments.

For this study, sediment cores were collected from three sites in the marina of Port Camargue on the French Mediterranean coast. This marina, the largest in Europe, was built around forty years ago and has never been dredged. Sediment samples (<63µm fraction), antifouling paints were analyzed for copper concentration and Cu isotope ratios. Isotopic measurements were performed using a Neptune Multi Collector ICP-MS after a double separation on anionic resin.

Copper concentrations in antifouling paints (7 different brands) ranged from 6 % w/w to 36 % w/w. Their δ65Cu values varies from 0.55 to 0.97‰. Close to the boat maintenance area, Cu concentrations in sediment cores exhibited an increase from the bottom to surface with a maximum value of 1961 µg.g⁻¹ at 7 centimeters depth. In parallel δ65Cu values increased from 0.08‰ at the bottom of the core up to 0.52‰ around 5 cm depth (Figure 1). This evolution toward δ65Cu values similar to those observed in antifouling paints in surface sediments, indicates that copper isotopes are good tracers of copper contamination by antifouling paints in a coastal marina.

Figure 1: Depth profile of δ65Cu and copper concentration in sediments from Port Camargue Marina.

Understanding the marine biogeochemical cycle of Pb in the equatorial Atlantic

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The biogeochemical cycle of Pb has been significantly perturbed by anthropogenic activity over the past 100 years, with transient changes in the relative importance of different anthropogenic Pb sources [1]. Lead isotopes are an effective tracer of anthropogenic Pb emissions, and the short residence time of Pb in ocean surface waters (~2 years, [2]) make them a useful recorder of recent Pb sources in a particular region. Furthermore, the comparatively conservative behaviour of Pb isotopes in intermediate and deep waters enables tracing advection of pollutant Pb [3].

A newly developed method, using TIMS in conjunction with a Pb double spike, has been applied to the measurement of the Pb isotopic compositions (206Pb/204Pb, 207Pb/206Pb and 208Pb/207Pb) and concentration of seawater depth profiles and surface seawater samples collected in the eastern equatorial Atlantic Ocean during the GA06 UK GEOTRACES cruise in 2011. The data are used to assess the current importance of anthropogenic versus natural Pb inputs to this region, and the advection of anthropogenic Pb into deep waters.

The Pb concentrations of surface waters (17-26 pmol/kg) are comparable to those determined in the early 1990’s in the region [4], suggesting a stable Pb flux over the past 20 years. The Pb isotope composition of surface waters between 8° N and 3° S (1.163-1.169, 207Pb/206Pb) are similar to those determined for Saharan dust [5]. In contrast, surface waters in the North Equatorial Current have higher 207Pb/206Pb ratios (1.173-1.174), a signature which can be attributed to advection of Pb from the west, fingerprinting eastern US emissions. A deep water maximum in Pb concentration (3000 m; 46 pmol/kg) located close to the mid Atlantic ridge is interpreted to represent hydrothermal input of Pb.


DOI:10.1180/minmag.2013.077.5.2

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Heavy metals characteristics in the gold and iron mine soils in the upstream area of Miyun Reservoir

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Metal contamination of soil from anthropogenic sources is an important global issue. Some recent studies have worked on the importance of metal contamination of soils in ecologically sensitive areas that are the source sites of drinking water. In this study, a preliminary survey of soil contamination had been carried out around the Miyun Reservoir, Beijing, China. Some results as follows: (1) the metal concentrations in the gold and iron mines soil samples exceed the background soil levels in Beijing, and the content of heavy metal in gold mine soils are higher than those of iron mine soils with Ti and Mn as an exception; the pollution of heavy metals in mine soils have reached a serious degree, and Hg is the most serious pollution element of all selected elements in gold mine soils. (2) Selected elements have been found the residual fractions is the most predominant in all gold and iron mine soil samples; the distribution of Ni in gold mine was similar to that of iron mine; Mn had the greatest acid-soluble portion (27.95% and 23.24%, respectively) reflecting that Mn was more mobile and potentially more bioavailable in the study areas; the acid-soluble and reducible portion of Cd (20.06%, 16.45%) in gold mine was significantly higher than that of iron mine (3.70%, 1.36%), and as well as Pb. (3) the selected heavy metals in both soil samples have different degrees of enrichment; the pollution degrees of gold mine soil samples was aligned to Pb>Hg>Cd>Cr>Cu>Zn>Co>As, while Pb>Cd>Cr>Co>Cu>Zn>Hg>As for iron mine soil samples.

Zn immobilization by Lumbricus terrestris calcium carbonate biomineralized granules

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Many species of earthworm secrete granules of calcium carbonate. In this study we investigated the incorporation of Zn into granules produced by the earthworm L. terrestris, cultured in an agricultural soil (Hamble) amended with Zn and a soil from a former Zn mine (Cwmystwyth, UK).

Bulk and µ-X-ray diffraction were used to determine granule mineralogy. Both vaterite and calcite were detected. Synchrotron µ-X-ray fluorescence (XRF) was used to determine the distribution of Zn within granules. Zn occurred in concentric zoning (Fig. 1) and as discrete hotspots. X-ray absorption spectroscopy was used to determine the Zn bonding environment within the calcium carbonate granules. The Zn exhibited several different speciations; replacing Ca in the calcite structure and as the minerals hydrozincite, Zn5(CO3)2(OH)6 and aurichalcite, (Zn,Cu)5(CO3)2(OH)6.

Figure 1: XRF map showing Zn distribution as concentric rims on the edge of a slice of a granule originating from Hamble soil amended with 750 ppm Zn. XRF average Zn concentration for this granule is 64 ppm and the bulk concentration from digested granules from this treatment is 164 ppm.

Zn is immobilized within biomineralized granules. Although, the degree of Zn uptake and granule production rates indicate that these biogeochemical processes have a less significant impact on Zn mobility compared to that for Sr [1] and Pb [2] at contaminated sites.

High sensitivity of ammonia and nitrite oxidation rates to nanomolar oxygen concentrations

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To date it remains unclear as to whether ammonia and nitrite oxidation can co-occur alongside and hence supply substrates for fixed N loss via either denitrification or anammox under nanomolar oxygen (O₂) concentrations. Both culture and field based studies have been restricted to O₂ concentrations greater than 0.25 µM. With O₂ concentrations regularly observed to be less then 10 nM in the core of oxygen minimum zones (OMZ) it is essential to assess the oxygen sensitivity of these processes at these levels.

Sampling was undertaken across the oxycline in the seasonal OMZ off Concepcion, Chile to determine rates of ammonia / nitrite oxidation from short-term incubations at manipulated O₂ levels between 5 nM and 20 µM. Rates of both ammonia and nitrite oxidation were detectable to the limit of our O₂ measurements and demonstrated a strong dependence on nanomolar concentrations of O₂. Michaelis-Menten kinetics fitted to this data produced half saturation constants (Kₘ) of 330 and 780 nM O₂ for ammonia and nitrite oxidation respectively. These values were consistent across multiple depths sampled in this study and are shown to be applicable across OMZ systems. These Kₘ values must be included in future modelling studies, in order to more realistically assess the impacts of ocean deoxygenation on nitrogen cycling.

Titration curves, column experiments, and reactive transport models

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Surface reactions related to e.g. transport and retardation processes in groundwater systems are correlated with geochemical conditions that vary in time and space. For long-term safety analysis of radioactive waste repositories it is of great interest to better understand and to realistically assess these geochemically driven surface and transport reactions, since they might strongly impact radiation exposure.

To get an advanced insight into these processes column experiments are conducted and subsequently modeled with the geochemical speciation code PhreeqC, Version 2.18 (coupled with UCODE_2005). In order to set-up realistic reactive transport models so-called surface complexation parameters (SCP) such as surface site density, specific surface area, and protolysis constants need to be derived from titration experiments of relevant mineral phases.

Two different titration techniques are conducted for muscovite and orthoclase: continuous and batch titration. Derived results are compared offering an insight into pH-influencing reactions that contribute to surface reactions but also to cation exchange and mineral dissolution.

In column experiments different solids are applied: natural sediments from the Gorleben site, Germany and pure mineral phases (orthoclase, muscovite, quartz). Parameters such as pH, ligands, ionic strength, and cation concentrations are varied in each experiment to reflect realistic environmental conditions. Moreover, transient pH conditions are applied in selected columns.

Both types of experiments (titration, column experiments) including each geochemical variation provide data to model reactive transport processes of hazardous pollutants more realistically in groundwater-flow driven environments with PhreeqC. Calculations will be conducted and first results offered for discussion.

This project is funded by the German Federal Ministry of Economics and Technology (BMWi) under contract no. 02 E 11072A and 02 E 11072B.
Recycled volatiles beneath the Western Antarctic Rift

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The Western Antarctic Rift System (WARS) represents an area of long lived extension between East and West Antarctica. The origin of this rift is poorly understood, with both an actively up-welling plume and passive rising of the asthenosphere being championed as the cause [1]. To explore the origin and evolution of the rift, a suite of 11 mantle xenoliths from Northern Victoria Land have been analysed for their halogen and noble gas isotopic signatures.

Noble gas and halogens are excellent tracers of volatiles within the mantle; providing a key source of information on the underlying mantle which is driving the rift. The fluid inclusions present within mantle xenoliths provide the best medium through which magmatic volatiles can be transported to the surface and still be able to retain a pristine magmatic signature. Noble gas and halogens contained within these fluid inclusions are released by in vacuo crushing and analysed through mass spectrometry.

Noble gas signatures extracted from the fluid inclusions show MORB like 3He/4He ratio of 7.4R A whilst the 20Ne/22Ne ratios are indicative of a deeper primordial mantle source. Halogen analysis has shown the samples to be extremely enriched in iodine with I/Cl ratios ranging from a MORB like 0.091 48 x 10 -3 to highly enriched value of 54.6 x 10 -3. These values are indicative of mixing between mantle and subduction fluid endmembers.

Halogen ratios indicate that seawater derived volatiles have been incorporated into the mantle during subduction. Volatiles were released from the slab at depth possibly by the breakdown of antigorite. This fractionated the halogens further causing an increase in the I/Cl ratio seen within the xenoliths [2]. Noble gas ratios indicate that the driving force of the rift is the convecting upper mantle, with an addition of a deeper mantle volatile source. Geochemical data, along with seismic evidence [3], suggests that slab detachment during the Cretaceous created localised convection currents which brought some primordial mantle up from depth. The rising mantle would have exerted a force on the bottom of the Antarctic Plate causing it to break apart.


Phototrophs and ore formation

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Sediments of the 1.64 Ga Barney Creek Formation (BCF) in northern Australia host one of the largest stratiform Pb-Zn deposits in the world. An early fraction of the zinc sulfide may have formed by discharge of zinc-rich fluids from a proximal fault into sulfidic bottom waters, causing synsedimentary precipitation of ZnS onto the sea floor (SEDEX model).

As the BCF contains the oldest known, thermally well-preserved molecular fossils (biomarkers) in the world, it is the ideal location to study the role of microorganisms and biogenic organic matter in this process. Solvent extracts of the sedimentary rocks yielded aromatic carotenoids produced by phototrophic sulfur bacteria, including extremely high concentrations of okenane from purple sulfur bacteria (Chromatiaceae) and chlorobactane produced by green-pigmented green sulfur bacteria (Chlorobiaceae) [1]. As okenone was exclusively known from planktonic Chromatiaceae, we envisaged a planktonic phototrophic community inhabiting a euxinic deep water system [2], consistent with a SEDEX component to ore formation. However, precursors of almost all fossil aromatic carotenoids have now also been discovered in microbial mats [3]. We present biomarkers from mat facies in the BCF and discuss whether the finely laminated sediments represent phototrophic microbial mats that thrived under a shallow, fully oxygenated water column or benthic mats that formed in a deep sulfidic basin.

Probing the water content of the Earth’s mantle: Hydrogen mobility under extreme conditions

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Research over the past few decades has shown that nearly all of the nominally anhydrous minerals (NAMs) of Earth’s mantle can incorporate substantial amounts of water as structurally bound hydrogen. This has important implications for understanding the geochemical and geophysical properties of Earth’s interior as the presence of water influences numerous mantle properties and processes. Water, as hydrogen, has been invoked to reconcile differences between conductivity models and geophysical observations of the mantle, but the amount present is yet to be satisfactorily quantified – with experimental estimates differing by several orders of magnitude. Hydrogen-deuterium exchange experiments performed under mantle conditions are presented, that provide data on hydrogen mobility in olivine directly comparable with electrical conductivity data. These results will be used in conjunction with existing estimates of conductivity and magnetotelluric survey data in order to constrain the water content and conductivity of olivine, and thus the upper mantle.


Evaluating proxies for oxygen fugacity at the Mariana arc

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Arc basalts are more oxidized than mid-ocean ridge basalts, but existing proxies for studying fO2 present contrasting explanations for this offset. The Fe3+/ΣFe ratio proxy indicates that the mantle wedge has higher fO2 than mid-ocean ridge source mantle. In contrast, trace element proxies (V/Sc, Zn/Fe*, and [Cu]) suggest that the fO2 of the upper mantle is uniform. Additionally, the Dvol/melt proxy suggests that arc magmas are oxidized at the time of high-Mg olivine fractionation. We present major and trace element concentrations and Fe3+/ΣFe ratios (µ-XANES) for melt inclusions and their olivine hosts from five Mariana arc volcanoes and Mariana Trough submarine glasses to compare the [Cu], Zn/Fe*, Dvol/melt, V/Sc, and Fe3+/ΣFe ratio proxies for calculating fO2.

The Zn/Fe* proxy returns Fe3+/ΣFe ratios of primary mantle melts and is sensitive to variations in Zn/Fe*source. After accounting for source composition, the Zn/Fe* proxy yields agreement with calculated primary Fe3+/ΣFe ratios for arc and back-arc glasses. Similarly, the [Cu] of arc melt inclusions are consistent with non-modal equilibrium melting of a source between QFM+1 and QFM+2, and fractional melting between QFM and QFM+0.5 for back-arc magmas. The V/Sc proxy returns more reduced primary fO2s than the Fe-based proxy for all samples, however fO2s for arc melt inclusions calculated using Dvol/melt (QFM+2.7 ± 0.3) are systematically more oxidized than their measured Fe3+/ΣFe ratios indicate (QFM+1.3 ± 0.3), suggesting that there may be a significant water, pressure, or source composition effect on the partitioning behaviour of V and Sc. These results show that the Fe3-, Zn/Fe*, and [Cu]-based proxies for fO2 are in broad agreement and are consistent with an arc mantle source that is more oxidized than mid-ocean ridge source mantle.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Petrogenesis of peraluminous granites from deep crustal sources

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The study of exhumed high-grade continental crust formed at convergent plate margins reveals important details about the petrogenesis of granites and contributes to a better understanding of processes responsible for the differentiation of the continents. The Fosdick migmatite–granite complex, West Antarctica, records evidence of two melting events, during the Devonian–Carboniferous and in the Cretaceous. A Devonian–Carboniferous calc-alkaline granodiorite suite emplaced into a Lower Paleozoic metasedimentary sequence (outside the complex) and their granulite facies equivalents (inside the complex) represent the sources and make this region ideal for the study of processes and mineral behavior during polycyclic anatexis at granulite facies conditions using a combined petrologic and geochemical approach. We report 20 new LA–ICP–MS U–Pb zircon ages extending the age ranges as follows: protolith granodiorite suite 377–339 Ma; Devonian–Carboniferous anatectic granites 369–350 Ma; and, Cretaceous anatectic granites 119–96 Ma. The discovery of Devonian anatectic granites suggests that melting occurred earlier than previously thought. New geochemical data for 48 samples extends a limited dataset from earlier work. The major and trace element geochemistry of paragneisses and orthogneisses is consistent with the hypothesis that they are the high-grade equivalents of the metasedimentary sequence and granodiorite suite respectively. The metasedimentary sequence has K2O of 2.15–4.32 wt%, Sr of 95–207 ppm and Rb of 96–216 ppm, whereas the calc-alkaline granodiorite suite has K2O of 2.23–5.01 wt%, Sr of 90–418 ppm and Rb of 88–381 ppm. Devonian–Carboniferous granites are either high Sr (225–363 ppm) or low Sr (95–108 ppm) types with variable K2O (2.73–6.85 wt%) and Rb (131–284 ppm). Cretaceous granites are either high Sr (207–298 ppm) or low Sr (90–167 ppm) types with variable K2O (3.21–8.89 wt%) and Rb (80–284 ppm). Limited isotope data indicates that Devonian–Carboniferous granites were derived primarily from the granodiorite suite, whereas Cretaceous granites were derived from mixed sources (the metasedimentary rocks, the granodiorite suite, or their high-grade equivalents). Additional Sr and Nd isotope and REE data currently being collected will better constrain the sources of the granites and allow an evaluation of the role of accessory minerals such as apatite and monazite during crustal melting events.

Beneficial uses of engineered nanoparticles and the behavior of natural and engineered nanoparticles in the environment

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Engineered nanoparticles (ENPs), including Ag(0), Au(0), C-nanotubes, ZnO, TiO2, Fe3O4, have many beneficial uses ranging from catalysts used for efficient production of chemicals (e.g., Au(0)) and photocatalytic degradation of organic pollutants (e.g., TiO2) to water treatment to remove As (e.g., Fe3O4) and use as antibacterial agents (e.g., Ag(0) and ZnO). Here we will review some of these uses, as well as some of the transformations that ENPs undergo in different environments (e.g., sulfidation of Ag(0) and ZnO ENPs), which can significantly alter their properties (e.g., solubility) and result in lowered risk. We will also review some of the lessons learned about the behavior of ENPs from microscopic studies of engineered and natural nanoparticles, in particular the sorptive properties of Fe3O4 ENPs in removing As from drinking water. We will also discuss some insights about the use of nanoparticles as environmental indicators gained from ab initio thermodynamics studies of the morphologies developed by NPs under different environmental conditions.
Geochemistry and mineral exploration

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Mineral exploration is a multi-disciplinary team effort, in which conceptual geological thinking and traditional geological field work play leading roles. Geochemistry, when properly integrated into the process, is a key component for exploration, from initial targeting through to resource definition.

Anglo American’s base metal discovery track record over the past decade (including ten significant discoveries) illustrates this point, where so-called conventional geochemical techniques played an important role in many of those discoveries.

Stream sediment geochemistry in areas of well developed topography, and soil geochemistry in areas of residual soil profiles are very effective techniques and played a role in the discoveries of the Morro Sem Boné Ni-laterite deposit, Brazil, and the Boyongan Porphyry Cu deposit, Philippines. In areas of thicker and/or transported overburden, surface geochemistry is unreliable, and Anglo American has preferred the more direct approach of drilling through the cover and sampling the base of regolith or top of bedrock (as used in the discoveries of the Gergarub Zn-Pb VMS deposit, Namibia, and the Sakatti Ni-Cu-PGE deposit, Finland). In addition to surface media geochemistry, lithogeochemical methods have been used in regional reconnaissance, and more locally for detecting distal effects of mineralisation, particularly around blind targets.

Fast and relatively cheap multi-element analysis by ICP-MS and computer software to aid interpretation have been the most significant technological advances over the last twenty years. More recently, portable XRF technology has enabled real-time decision-making in the field.

Anglo American actively supports geochemistry-related R&D through engagement with several key research centres globally (e.g., CODES and MDRU), and funding of PhD students. Strategic alignment of research objectives with the long term needs of industry is a key challenge, as is the gap in undergraduate teaching in applied exploration geochemistry at universities.

The fate of Archean primary crust and the transition to subduction

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Petrological data and thermal models indicate Archean mantle potential temperatures ($T_p$) were up to 240°C hotter than at present, but with a similar variation (~100°C). Higher $T_p$ generated thick MgO-rich ultramafic primary crust (PC) and highly residual lithospheric mantle (LM). Subduction and plate tectonics were unlikely. The preserved volume of PC is low suggesting that most is missing, which we address by modelling the equilibrium mineral assemblages for a range of metamorphosed (hydrated) PC compositions and complementary residues for a Moho $T$ of 1000°C. We use calculated compositions of primary melts and complementary residues of high-MgO non-arc basalts as proxies for the secular change in composition of PC and LM. The density of LM decreases slightly with increasing $T_p$, whereas that of PC increases dramatically. The base of PC with MgO >21–22 wt%, produced at $T_p$ >1600°C, was unstable at crustal thicknesses >45 km (>1.5 GPa), even when fully hydrated. Archean low-MgO eclogites and TTGs were derived from basaltic compositions and require that the PC was fractionated. Although the thermal structure of the mantle in the Hadean and Eoarchean is poorly constrained, heating from radioactive decay exceeded surface heat loss in the interval before 3.0 Ga and Archean geodynamics was probably variable, controlled by the spatial range in $T_p$. This regime was likely dominated by delamination/convective downwelling of PC that may have partially melted to produce basalt or refertilized the underlying mantle causing additional melting and crustal thickening. The resulting magmatic additions form plateau-like crust. Archean continental crust is dominated by TTGs. Collision of plateaux and/or plateaux overriding PC lithosphere was responsible for inducing melting to generate this TTG crust. Post 3.0 Ga tectonics was dominated by the onset of subduction, plate tectonics and a transition to the supercontinent cycle, consistent with the dominance of secular cooling since 2.5 Ga, and the rare occurrence of paired metamorphism and scarcity of eclogite in orogenic belts from the Mesoarchean to Paleoproterozoic. The onset of subduction may have triggered an overturn of the LM, as evidenced by $T_{rd}$ model ages for the LM.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
**Mutiple isotopic tracers to monitor remediation of uranium solution mining**

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Roll front uranium deposits form by interaction of U-bearing groundwater with reduction-oxidation gradients in the host sediments. This redox gradient in many roll-front deposits can be visually identified by hematite staining on the oxic side and green-gray sediment color on the anoxic side. A dark boundary between these two zones is concentrated in U(IV) minerals and other reduced metals such as Se and Mo. Solution mining of roll-front deposits perturbs natural redox conditions by oxidizing U (and other metals) in the main ore body for economic recovery. This perturbation coupled with an extensive monitoring well network provides a unique opportunity to assess the natural recovery of reducing conditions after the cessation of mining as a remediation strategy.

We have conducted a characterization survey of groundwater, mining fluids and complimentary ore body sediment core from the Smith Ranch mine in eastern Wyoming, USA for $^{87}$Sr/$^{86}$Sr, $\Delta^{34}$S sulfate, $\delta^{234}$U and the $\delta^{234/238}$U activity ratio. Sampling locations include both active and inactive mining sites. Monitoring wells surrounding the ore body have 4-22 ppb U, 68-413 ppm SO$_4$, $\delta^{234/238}$U activity ratio 2.9-5.5, $\Delta^{34}$S -16.6--10.8, $\delta^{234}$U/$^{238}$U is between 0-2 for most samples.

Acid leachates of sediment core from a previously mined unit have low $\delta^{234}$U/$^{238}$U activity (0.6-1.6) compared to groundwater outside the ore zone. $\Delta^{34}$S spans nearly 52% (-48-+3.8%) and most samples have $\delta^{234}$U/$^{238}$U between -2 and 0%. The depletion of $^{234}$U in dissolved U(VI) as indicated by negative $\delta^{234}$U/$^{238}$U suggests U(VI) reduction in the groundwater. There are no observed correlations between $\delta^{234}$U/$^{238}$U activity and $\delta^{234}$U/$^{238}$U. However the U activity ratio does correlate with depth. The low ($\delta^{234}$U/$^{238}$U) in the ore zone will be a sensitive tracer for quantifying the migration of ore zone U to uncontaminated groundwater.

**Iron availability controls phytoplankton ecophysiology in the South Atlantic Subtropical Convergence Zone**

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Measurements of phytoplankton photophysiology using Fast Repetition Rate fluorometry (FRRf) from the UK-GEOTRACES 40°S Atlantic cruise (GA10; JC068) have characterized two dominant ecophysiological regimes which are interpreted on the basis of nutrient limitation. South of the South Subtropical Convergence (SSTC) in the Antarctic Circumpolar Current (ACC) of the Eastern Atlantic Basin, waters are characterized by elevated chlorophyll concentrations, dominance by larger phytoplankton cells, and low $F_{v}/F_{m}$ values. The reason for the low $F_{v}/F_{m}$ values was iron (Fe) limitation, which was confirmed via 24 hour on-board Fe addition incubation experiments. Fe supply to these waters, either through artificial bottle additions or natural downstream enrichment from Gough Island in the Central Atlantic, resulted in significantly increased $F_{v}/F_{m}$. Satellite images suggest a broader region of enhanced chlorophyll concentrations around the SSTC of the Western Atlantic relative to the Eastern Atlantic, which is hypothesised to be a result of higher iron supply from the South American continent. To the north of the SSTC at the southern boundary of the South Atlantic Gyre, phytoplankton are characterized by high values of $F_{v}/F_{m}$, which coupled with the low macronutrient concentrations and increased presence of picocyanobacteria, are interpreted as conditions of Fe replete, balanced macronutrient-limited growth.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Seismic anisotropy as a constraint on composition in the lower crust
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Our current interpretation of the composition of the middle and lower crust comes mainly from seismic observations, yet it remains a challenge to link seismic observations directly to composition. This is because isotropic seismic properties are similar across a range of compositions. Taking anisotropy into account allows for further refinement of our interpretation of composition provided that anisotropy is characterized for candidate rock types. This study uses electron backscatter diffraction (EBSD) measurements of crystallographic preferred orientation of minerals to calculate seismic anisotropy in samples of the Pelona-Orocopia-Rand (POR) schist from the Mojave region of southern California. The goals of this work are to characterize the seismic anisotropy of the POR schist and its relationship to observed lower crustal anisotropy in the region, and to refine predictions of lower crustal composition based on seismic anisotropy.

Velocity anisotropy in individual samples of the POR schist ranges from ~2–11% in Vp and ~3–15% in Vs, which is consistent with results of [1] for lower crustal anisotropy in southern California. When all schist samples are averaged together, the velocity anisotropy is significantly reduced to ~6% in Vp and ~8% in Vs. The symmetry of Vs anisotropy is roughly uniaxial with a unique slow axis perpendicular to foliation for all samples. Samples with significant modal quartz or amphibole have near orthorhombic Vp symmetry with slow velocities perpendicular to foliation. Maximum Vp is ~parallel to lineation, except in samples with significant quartz displaying prism-<a> slip; for these sample Vp-max is parallel to foliation, perpendicular to lineation. Modal quartz content is inversely correlated to isotropic Vp/Vs ratios, and mica and amphibole are positively correlated with anisotropy. Relative mica/amphibole contents can be distinguished using a combination of isotropic Vp, and Vs anisotropy. Quartz content can be estimated from Vp/Vs ratios.

[1] Porter et al. (2011), Lithosphere, 3, 201-220

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org

Pockets of Proterozoic hydrocarbons and implications for the Archaean
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Precambrian biomarkers convey invaluable information about the early evolution of life, ancient ecosystems, redox conditions, climate and depositional environment and prospective petroleum systems. They are however thermally unstable, easily obliterated by contamination and thus extremely difficult to find. This is particularly true if conditions favourable for biomarker preservation had to prevail for more than 2.5 billion years – the prerequisite for finding Archaean biomarkers. Many organic geochemists abandoned this hope after original discoveries of Archaean biomarkers proved to be of younger origin [1,2] but our study of ca. 550-825 Ma old sediments from the Centralian Superbasin now shows that biomarkers can be preserved in distinctive pockets in seemingly barren areas, even if sections are metamorphosed in parts. Most Centralian sections seem empty. Yet, eventually we identified intervals with preserved biomarkers in three drill cores. A detailed investigation of 825 Ma sediments in drill core Mt Charlotte-1 revealed maturity variations that are most likely due to hydrothermal influence and in turn control the hydrocarbon preservation. Sediments might appear metamorphosed after localized, subtle alteration by hydrothermal fluids but protected intervals can still contain biomarkers. The same might be true for Archaean sediments and we might still find those protected intervals with indigenous biomarkers that allow us to glimpse the early life on earth.

Evidence for melt accumulation in the subridge melting region:
A mantle residua perspective

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Melt extraction from the mantle has been shown to be driven by channelization favoured by melting of source heterogeneities possibly leading to melt accumulation both on- and off-axis1. Here we present a REE study of clinopyroxene in residual abyssal peridotites showing that melt extraction rarely follows fractional melting trends at the typical dredge haul scale (<1 km). Instead local melting trends reveal REE pattern evolution usually driven by infiltration of relatively enriched melts frequently accompanied by melt accumulation. Estimated compositions of the infiltrating melts suggest they derive by mildly enriched heterogeneities and/or grt-field melting of a DMM-like source2. Observed data can be modelled by open system melting in which instantaneous melts represent the mix of influxing and locally generated melts and where the melt exceeding the critical mass porosity escapes. The out coming scenario shows a possible intermittent behaviour where melting switches from near-fractional to near-batch. In open system melting this behaviour is imaged by fluctuations of the critical porosity/degree of melting value, where the critical mass porosity is a proxy of the accumulated melt fraction.

Lower thermal settings and spreading rates could favour the retention of the compositional trends associated to fluctuations in the melting regime. Accordingly, we found that the statistical distribution of REE trends accounts for a more effective melt accumulation and enriched melt infiltration along the South West Indian Ridge with respect to the Mid Atlantic Ridge.


Lifestyles of the slow and lonely –
A story told by sulfate isotopes

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Sulfur is a bio-essential component of any living organism and is at the same time heavily used by microbes for energy yielding (dissimilatory) processes. Dissimilatory sulfate reduction (DSR) coupled to the oxidation of organic matter plays a pivotal role in the re-mineralization of organic matter in marine sediments, which is owed mostly to the high concentration of sulfate in the overlying seawater relative to other energetically more favorable electron acceptors such as oxygen or nitrate. When sulfate is depleted methane becomes the end product of organic matter degradation. At the interface between downward diffusing sulfate and upward diffusing methane (sulfate-methane transition) sulfate is consumed by sulfate reduction coupled to the anaerobic oxidation of methane (SR-AOM). In the classic view, DSR is thus confined to the main sulfate zone, a redox zone where the more favorable electron acceptors are absent.

Thanks to new findings, such as i) the discovery of sulfate generation in methanic sediments well below the main sulfate zone, the so-called “cryptic sulfur cycle” (Holmkvist et al. 2011 [1]), ii) the discovery that SR-AOM utilizes biochemical pathways different from DSR (Milucka et al. 2012 [2]) and iii) the discovery of sulfur oxidation by cable bacteria (Pfeffer et al. 2012 [3]) our view on sedimentary sulfur cycling has recently been dramatically changed and broadened.

Stable sulfur and oxygen isotope tracing of these newly discovered processes in the environment and in the rock record could provide us with compelling insights into these so far unrecognized biochemical sulfur transformations. However, there is a complication/caveat: we do not yet know what isotope signature we should look for.

I hypothesize that the sulfur and oxygen isotope effects of oxidative and reductive sulfur cycling mediated by microbes in the deep biosphere – organisms that live a slow and lonely life – may provide clues to what isotope signatures to expect.

Chances and challenges in applying sulfur-oxygen isotope relationships of sulfate to studying sulfur cycling in engineered environments

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In recent years, our understanding of the mechanics of sulfur and oxygen isotope fractionation by sulfate reducing microorganisms has drastically improved. Based on multi-step sulfate reduction models, we are not only able to answer the question of why there is a large range of sulfur and oxygen isotope fractionations related to this process, but can also predict sulfur-oxygen isotope fractionation relationships (Brunner et al. 2012 [1]).

While this progress is exciting, it does not automatically provide new insight into sulfur cycling in perturbed ecosystems, such as polluted soils and aquifers, sites where sulfate reduction can be anthropogenically stimulated as a means to remove or sequester organic and inorganic contaminants.

Such systems are often highly complex because they are affected by different modes of microbial and abiotic sulfur cycling (i.e., reductive and oxidative processes), non-steady state conditions, and by mixing of waters from different sources. Additional challenges arise from the fact that monitoring of such systems is typically restricted to a few sampling points and cannot be carried out continuously.

Despite these complications, by comparing the combined sulfur and oxygen isotope signature of sulfate to the predicted sulfur-oxygen isotope relationship for sulfate reduction, it should be possible to tease out crucial information about sulfur cycling in engineered ecosystems, such as the extent to which sulfate is reduced, and the extent to which reduced sulfur is re-oxidized to sulfate.

Approaches where natural abundance sulfur and oxygen isotope signatures are combined with the outcome of stable isotope tracer experiments and evaluated by comparison to numerical models yield promising results. However, such modeling efforts can only yield meaningful conclusions when appropriate model assumptions are chosen. The evaluation and definition of these assumptions may prove to be the biggest challenge in deciphering sulfur cycling in engineered environments.

Metal isotopic distributions in mycorrhizal trees: Weathering manifestations and within-plant fractionations

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Although it is well known that organisms contribute significantly to the weathering process and to the distribution of elements within continental environments, the degree to which biota actively drive weathering versus the degree to which organisms benefit from nutrients released during largely inorganic weathering processes remains unknown [1]. Furthermore, the relative influence of different organisms on key elemental cycles, such as the base cations, especially Ca and Mg, is poorly understood. To address these questions, we have carried out a series of geochemical studies on semi-hydroponically cultured trees (Pinus sylvestris, Acer saccharum and Betula alleghaniensis) grown with appropriate mycorrhizal symbionts (ectomycorrhizal or arbuscular) in different geologic substrates (carbonate versus granitic) and under different nutrient regimes (N-limited in high or low nutrient supply and P-limited). Plant tissues across these biogeochemical experiments were studied for elemental abundances and Pb, Ca and Mg isotopic signatures. We conclude from our approach that: (1) Pb isotopes effectively complemented elemental signatures to identify key mineral dissolution reactions (e.g., the dissolution of phosphate phases in P-limited cultures); (2) for the same geologic substrate, arbuscular fungus did not demonstrate substantive phosphate dissolution; (3) the presence of mycorrhizal fungus significantly affected the Ca and Mg elemental distributions within the plant tissues but had a more muted effect on the Ca isotopic distributions; (4) foliar and root tissues recorded distinctive isotopic compositions (e.g., differences up to 0.6 ‰ 44Ca); and (5) ectomycorrhizal symbioses may drive Mg isotopic variations during weathering.


Nanomagnetism of iron meteorites identified by X-ray photo-emission electron microscopy
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Paleomagnetic signals stored within meteorites are a key source of information regarding many processes in the early solar system. An increasing body of traditional macroscopic paleomagnetic evidence suggests that, while molten, the liquid cores of the meteorite’s parent asteroids generated magnetic fields with comparable strength to those of present-day Earth. We have applied nanoscale magnetic techniques to show that spinodal nanostructures within meteorites are capable of providing a time-resolved record of dynamo activity of their parent asteroids - analogous to that stored in the Earth by the spreading ocean crust - across the first 100-200 Ma of the asteroid’s history, a prospect that could revolutionise our understanding of asteroid development.

To investigate this magnetic nanostructure, we performed the first meteoritic high-resolution X-ray photo-emission electron microscopy experiments (on the Tazewell IIICD iron meteorite). The results display a distinct and unique magnetic pattern that is dependent on the underlying nanostructure. The spinodal region, termed the ‘cloudy zone’ (CZ), extends 2-10µm and is composed of tetrataenite (chemically ordered FeNi) embedded in a hitherto unobserved ordered Fe3Ni phase. Within this region, a complex magnetic state is observed with interlocking groups of all three tetrataenite twin orientations. A clear variation in the amount of each twin with increasing lateral distance across the CZ (decreasing age of tetrataenite formation) is also present. The observed magnetisation pattern bears resemblance to anti-phase boundaries (APBs) that appear to coarsen over time. These results provide both a fundamental understanding of the CZ magnetisation as well as the magnetic state formed in the absence of a dynamo field. Chondritic meteorites can carry an analogous magnetic remanence that was influenced by a dynamo field. By comparing the results in this study to those of chondritic meteorites, we will identify both the direction and magnitude of this dynamo field over a 100 Ma period.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Experimental and theoretical study of malachite solubility in ammonia aqueous solutions

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Experimental and theoretical investigations of malachite solubility was carried out as a part of search of copper carbonates (malachite and azurite) crystallization conditions [1]. The solubility of CuCO₃•CuOH₂ was studied experimentally in 1.0, 2.0, 3.0 m ammonia solutions at temperatures of 25, 50, 75°C. Moreover, thermodynamic calculations were performed for indicated ammonia concentrations and temperatures. An initial material was placed in ampoules made of thermal-resistant glass, then it was grouted of ammonia solution of necessary concentration. The ampoules were sealed and placed into thermostat. After equilibrium the ampoules were unsealed, and an aliquot part of the solution was filtered and analysed for a total copper content. We used the volumetric iodometric method for estimation of the copper content and a total CO₂ content in solution was determined using AN-7529 express-analyzer.

The experimental study have shown that the equilibrium copper content increases with ammonia concentration increasing and decreases with temperature rise in ammonia solutions. Malachite is unstable in the ammonia solution at given condition it decomposes with tenorite forming, that was confirmed by the thermodinamic calculations. The results of the thermodimamic calculations and the experimental study of malachite solubility has a satisfactory fit in general (Fig.1).

Figure 1: Calculated and experimental data of malachite solubility as functions of NH₃ concentration and temperature.


Geochemical processes affecting stream water at European scale investigated by differential scaling operator (perturbation) in the simplex metric

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Compositional data consist of vectors whose components are parts of some whole. Their statistical analysis performed in the real Euclidean sample space is not able to capture their features. Data in fact lies in a constrained space, called simplex, where to characterise the difference, or changes from one composition to another, specific operators have to be considered. In this contribution, perturbation, the group operator working in the geometry of the simplex sample space [1], is applied to analyse the differences in the chemical composition of the solutes of stream waters at European scale [2]. The analysed data are from the FOREGS (Forum of European Geological Survey) [3] database. New numerical and graphical tools are proposed to investigate the behaviour of elements or chemical species in the constrained space. In the FOREGS project, running stream waters were collected from the small, second order, drainage basins (<100 km²) at the same site as the active stream sediments. Starting from the analytical results matrix, chemical data of some selected variables, considering their geochemical affinity, were ranked by taking into account their conducibility values. Perturbation vectors from one composition to the subsequent one are calculated and results plotted in variation diagrams. The aim is to investigate the relative behaviour of the ions and chemical species, as well as the effect of weathering and dilution processes on a European scale, by considering the use of calculus ooperators working in the simplex geometry. The possibility to model processes at the base of the distribution of chemical elements/species (e.g., presence of trends depending on space, chemostatic behaviour, …) is also explored.

X-ray study of high pressure induced densification of lithium disilicate glass

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Lithium disilicate glass (Li₂O.2SiO₂) is a very interesting vitreous material, because, besides several important technological applications (e.g. biomaterial to produce prostheses and implants), shows a large difference between the Tg and Tc values. This is important for the investigation of the crystallization mechanism on vitreous phases, as it allows the independent study of the nucleation and growth stages. In this work, we have investigated the effect of high-pressure processing in the induction of structural changes in the amorphous phase. This can give place to polyamorphism and/or to the generation of possible seeds for a crystalline phase nucleation. Using toroidal type high-pressure chambers, glass samples were processed at 2.5 GPa, 4 GPa, 6 GPa and 7.7 GPa at room temperature. X-ray diffraction using synchrotron radiation was used to obtain the radial distribution functions in order to follow the structural changes at different ranges. Compared to a pristine sample, the main change observed for the samples processed up to 6 GPa was associated to the distortion of the SiO4 tetrahedra, as already observed in the literature. However, for the sample processed at 7.7 GPa, we have identified a drastic change in the RDF, which points for the production of a different amorphous phase with a local structure closer to that observed for the Li₂SiO₃ crystalline phase.

The 15N and 18O isotopic signature of abiotic reduction of nitrite by iron

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Evidence is mounting for the importance of interactions between reactive intermediates of multiple elemental cycles. For example, while previous studies have shown that oxidation of Fe(II) by nitrate (NO₃⁻) and nitrite (NO₂⁻) – a reactive intermediate of both reductive and oxidative N cycling processes - the controls on these reactions in the environment are poorly understood. Moreover, the N product of abiotic, anaerobic NO₂⁻ reduction by Fe(II) can include nitrous oxide, nitric oxide, ammonium or dinitrogen gas – yielding a myriad of implications for the fate of N across all types of ecosystems. Furthermore, we posit that these types of reactions may represent an important control on the dual NO₃⁻ and NO₂⁻ isotopic composition in Fe-rich, reducing environments low in organic carbon (e.g., aquifers). To date, however, the kinetic isotope effects of these processes remain uncharacterized.

Here we present the first investigation of the dual isotope systematics of abiotic NO₂⁻ reduction by Fe(II) under a variety of environmentally relevant pH values and reactant concentrations. In our experiments, we observe a rapid decrease in NO₂⁻ postively correlated with Fe(II) concentrations, followed by a second phase of slower NO₂⁻ reduction, possibly implying the involvement of secondary Fe(II)/Fe(III) mineral phases. Samples were collected for NO₂⁻ N and O stable isotope analyses in order to determine the isotope effects associated with abiotic NO₂⁻ reduction by Fe(II). As many studies suggest a potential for anaerobic, abiotic nitrogen transformations coupled with iron cycling, the N and O isotope effects determined here will be helpful for using dual isotopes of nitrite (and nitrate) to decipher the biogeochemical fate of N in host of important environments including soils, sediments, wastewater treatment plants and aquifers.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Evaluation of atmospheric flows of mineral substances in the northeastern coast of Baikal Lake during the last 200 years

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Oligotrophic bogs are capable to maintain in its peat deposits the mineral substance of atmospheric aerosol. The study of microelement composition of the stratified horizons allows us to determine the changes in chemical content of atmospheric aerosol under the influence of natural and anthropogenic factors in the historical time.

Dulihinskoe bog, located in the territory of the Baikal State Biosphere Reserve, took our attention as an object for retrospective geochemical monitoring. In the center of the bog (N 51°31’, E 105°00’) there were selected the top 47 cm of the 4-meter peat packs of 11000 years old [1] in the form of the monolith with square 22 * 13 cm². There was defined 4-meter peat packs of 11000 years old [1] in the form of the contrast to the Western Siberia with its arid environments.


Evaluation of the Lu-Hf-in-lawsonite geochronometer

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We present an evaluation of the recently established Lu-Hf-in-lawsonite geochronometer [1, 2] including a reliable separation procedure for lawsonite. For this purpose, four blueschist-facies rocks from the island of Syros (Greece) and the Tavanli Zone (Turkey) were investigated, covering a wide range of different lawsonite occurrences, as well as pseudomorphs after lawsonite.

The developed mineral separation procedure involves magnetic and density separation as well as hand-picking and yields almost pure lawsonite concentrates. Lutetium and hafnium concentrations as well as Hf isotope ratios were obtained by using a selective digestion technique for mineral separates [3], a single-column separation procedure for element purification by ion exchange [4], and high-precision isotope ratio measurements by MC-ICP-MS.

Lawsonite showed elevated Lu concentrations of 0.4-1.4 ppm and very low Hf contents of <0.1 ppm. The 176Lu/177Hf values of 0.6-4.4 are comparable to other minerals used for Lu-Hf geochronology and allow obtaining well-defined isochrons and precise ages. However, bulk pseudomorphs after lawsonite do not preserve the Lu and Hf concentrations or Hf isotope ratios of the former lawsonite after its prograde breakdown. The obtained Lws-WR age (50.3±1.2 Ma) of the HP-LT metamorphism on Syros is in excellent agreement with previously published geochronological and geothermobarometric studies [e.g., 3]. The Lws-WR ages (87.5±1.1 Ma, 89.3±1.8 Ma) of two metabasites from the Tavanli Zone provide the first tight constraints on the onset of HP-LT metamorphism in this region [e.g., 5].

Due to its relatively small P-T stability range and elevated Lu/Hf values, lawsonite is well suited for Lu-Hf geochronology and has proven to be a powerful tool to date high pressure-low temperature metamorphic events. This geochronometer allows dating lawsonite growth in rocks of the lawsonite-blueschist subfacies and offers numerous prospects for investigating different subduction zone processes.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Method for measurement of argon isotopes in helium flow for K/Ar geochronology

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We present a method for the measurement of argon isotopes in the potassium-argon (K/Ar) geochronology of the controller based on the series (conventional) mass spectrometer operating in dynamic mode. Installation for the quantitative measurement of isotopes of argon laser system has a sample preparation, based on CO₂ laser, where the isolation and purification of argon is in a continuous flow of ultra-pure helium. The system is based on the mass spectrometer MAT-253 (Thermo Scientific), equipped with the detectors Faraday m/z 36, 37, 38, 39 and 40 and use chromatographic purification system.

Instead of the traditional method of isotope dilution of 38-argon method is comparing the signals from the sample gas and gas-standard of known isotopic composition (by air) before and after the measurement of each sample. This method, using of air argon as the reference gas has an advantage over conventional method of 38-Ar isotopic dilution there is no contamination of the sample by 40Ar/36Ar incoming from a tracer 38-argon a quantity of argon in a dose is invariable for several years; availability of 40Ar/36Ar air ratio monitoring by reference gas.

A sample is placed in multi-charge chamber. The chamber contains 10 to 35 samples, depending on the size. To release the argon from a sample the CO₂ laser is used. The gas that was released during fusing, primary treatment is the U-shaped trap, placed in liquid nitrogen. Next argon helium flow passes through the capillary chromatography column for purification of argon from contaminants.

This method is an alternative method for measuring the argon isotopes in the potassium-argon (K/Ar) geochronology of the static mode and can be used for analysis of radiogenic argon N * 10⁻¹² g with the same sensitivity and accuracy, the method is simpler and more reliable. Small amounts of radiogenic argon extracted from geological samples require high stability, low backgrounds, minimal content of argon in the blank experiment, and high sensitivity of the isotope ratio mass spectrometer.

The presented method has been successfully used to solve geological, geochronological and geoarchaeological issues.


GIS mapping of geological features of the Baikal mountain region based on integrated geochemical indicators

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Baikal mountainous area and Kodar-Udokan structural-formational zone are perspective to search for deposits of noble and rare metals. The studies 2009-2012, the authors created a spatial database including geological and geochemical information for the various objects of the ore zone. For the analysis of this information is required to cartographically display more than 50 layers of geochemical data. Classical overlay-based GIS representation of such a large data set makes it difficult visual analysis. The authors found some mathematical and geographical distribution patterns of useful component that allowed the development of mathematical tools, providing spatial calculations of integrated geochemical indicators - "modules", which are comprehensive indicators of certain ore-forming processes. Form of their representation is suitable for GIS-mapping.

For example, the figure shows the calculation of Eu/Eu * module. Well traced the species change of rocks of different stratigraphic levels, to lying on each other. This approach provides the ability to make geological conclusions, based on visual analysis of only 5-7 data overlays. Created GIS software can serve as a navigator geochemical exploration.
Quantifying more than half the periodic table of elements in uranium ore concentrates:
Results of the IAEA’s interlaboratory comparison 2011-2012, and two new quality control materials

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The analysis of trace elements (impurities) in uranium ores and uranium ore concentrates (UOC), as well as uranium-bearing materials in general, is performed in a variety of fields, e.g., in geochemical research, for quality control in the production stream converting uranium ores to nuclear fuel, as material signatures in nuclear forensics, or in international nuclear safeguards to support the verification of States’ declarations.

An interlaboratory comparison on the quantification of impurities in UOC was organized by the International Atomic Energy Agency (IAEA) during 2011-2012. The goal was to probe the analytical capabilities of the participating laboratories (i.e., the current state-of-the-practice), to determine any differences between laboratories and their potential causes, to identify chemical elements that are problematic and/or difficult to analyse with established analytical techniques, and to assess the measurement uncertainties. Six participating laboratories were tasked to quantify 69 impurity elements – more than half the periodic table – in two different UOC materials. The impurity concentrations, normalized to uranium content, covered more than six orders of magnitude. Inductively-coupled plasma mass spectrometry (ICPMS) was the main technique used by the participating laboratories.

A summary of the comparative results will be presented, highlighting the current state-of-the-practice in ICPMS analytical approaches as employed by the participants. Lessons learned, including the identification of polyatomic interferences and the challenge of estimating measurement uncertainties, will be discussed. This interlaboratory comparison yielded consensus values for the two UOC materials. They are suitable for future use as quality control materials addressing gaps in the availability of reference materials for impurity elements in uranium-bearing materials.

C, N₂, Ar, He in fluid inclusions in a garnet lherzolite from Oasis Jetty, East Antarctica

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To reveal the sources and evolution of fluids during mantle metasomatism under East Antarctic we have carried out optical, thermobarogeochemical and Raman-spectroscopy investigations and studied C, N, Ar and He isotopic and elemental ratios in Px separate from Oasis Jetty garnet lherzolite by stepwise crushing method. The sample contains abundant fluid inclusions of different generations and compositions. The applied methods have revealed two major fluid activity stages. The early stage fluid inclusions are characterized by the most complex composition and high pressures (>13 kbar), some of them reach 10 µm in size. The late stage fluid inclusions (P ≥ 5-7 kbar) are all very small (2-5 µm and less); the predominance of CO₂ over all other gases is dramatically increasing in them, as well as the role of H₂O.

Our isotope-geochemical data confirm the existence of these two fluid sources. The high pressure and larger size fluid inclusions of the early stage mostly opened at the very first crushing steps are characterised by low C/N₂, C/Ar, N₂/Ar (31-34) ratios, typical for the MORB chilled glasses δ¹³C values in CO₂ (-4.7‰), heavy nitrogen (up to +2.05±0.28‰), and slightly elevated ⁴₀Ar/³⁶Ar ratios (up to 533±10). The late stage fluid inclusions being progressively opened with increasing number of strokes are better characterized by the gases extracted at the very last crushing steps. They have 2-3 orders of magnitude higher C/N₂ and C/Ar ratios, close to the atmospheric N₂/Ar (86) and ⁴₀Ar/³⁶Ar ratios (down to 370±7), lighter δ¹³C values in CO₂ (down to -6.8‰), and nitrogen (-2.28±0.26 ‰). The elemental and isotope ratios (N₂/²⁰Ar, ⁴₀Ar/³⁶Ar, *He/²⁰Ar*, δ¹³N) correlate to each other, reflecting mixing between early and late stage fluids. The letter is the result of a mixture between MORB-type mantle and atmospheric components. The early stage fluids could be the result of more complex mantle-crustal components mixture with high proportion of atmosphere derived argon. Typical for intra-plate mantle xenoliths element fractionation due to fluid-melt partitioning is observed in low *¹He/²⁰Ar* ratios (0.1-0.7, compared to the mantle production ratio of 1.5-2). Some isotope fractionation (for N₂ and C) also could not be excluded.
Radiometric $^{81}$Kr dating reveals 120,000 year old ice at Taylor Glacier, Antarctica

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Ancient ice can not only be obtained from deep ice cores, but also at ice sheet margins and blue ice areas (BIAs) where it outcrops due to local ice dynamics and surface ablation [1]. Determining an accurate chronology for BIA records is more challenging than for regular ice cores. Here we report the first successful $^{81}$Kr radiometric dating of ancient BIA ice. $^{81}$Kr ($t_{1/2} = 229$ ka) is produced cosmogenically in the upper atmosphere, and the modern $^{81}$Kr-Kr ratio is used as the reference. Krypton is not reactive and is well mixed in the atmosphere. In principle $^{81}$Kr dating can be used to date ice in the 50ka to 1Ma age range; it is widely applicable as all glacial ice contains trapped air; it does not require a continuous or undisturbed ice stratigraphy; and it does not suffer from in situ cosmogenic production in the ice (as is the case for $^{14}$C). The large sample size requirement (> 40 kg) has precluded its use in ice core science to date.

Air was extracted on site from four 250 kg polar ice samples obtained from 5-15m below the surface of Taylor Glacier, McMurdo Dry Valleys, Antarctica. Krypton was separated from the air and dated using Atom Trap Trace Analysis [2]. The $^{81}$Kr radiometric ages agree with independent stratigraphic dating techniques within 6ka. $^{81}$Kr analysis shows that the samples are free of modern air contamination, validating our sampling strategy and experimental methods. We show that ice from the Eemian interglacial (130-120ka BP) can be found in abundance near the surface of Taylor Glacier. Our study paves the way for reliable radiometric dating of ancient ice in BIAs and margin sites, greatly enhancing their scientific value as archives of old ice and meteorites. As sample size requirements continue to decrease, ice core $^{81}$Kr dating might be a future possibility.


Geochemical types of tantalum and niobium mineralization from the rare metal-bearing granites and pegmatites of the Western Mongolia

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Tantalum-niobates are typical representatives of the rare metal mineralization in Middle Paleozoic and Early Mesozoic pegmatites and amazonite granites of the Western Mongolia (the Mongol Altay, the Charchirinsk upland region). They are seen in association with beryl in pegmatites, and characterized by heterogeneous composition of minerals, which is displayed in variability of Ta/Nb ratio from 0.3 to 3.0 from the grain core to boundaries. Tantalum-niobites in granites have microscopic sizes (2.5-150 μm) and are present as poikilitic inclusions in rock-forming minerals of protolitsonite-microcline-albite paragenesis, more rarely in accessory fluorite and magnetite. At the same time, tantalum niobite grains are chemically homogeneous, but differ from each other by various Ta/Nb (0.03-0.4) and Ti/Nb (0.02-9.8) ratio, as well as significant content of LREE (20 wt.%), Sn (up to 4 wt.%). Ilmenorutile (Ta+Nb from 3-12 to 23-27 wt. %), columbite-(Mn), columbite-(Fe), tantalite-betafite, betafite, and polycrase were defined in the rocks studied. These elements show acid-base conditions for mineral-forming environment. Changing alkalinity during pegmatite crystallization is noted within some zonal minerals as transforming of columbite into ilmenorutile (Ta/Nb-1.3; Ti/Nb-3.1), and tantalite-betafite (Ta/Nb 2.5 to 3.0; Ti/Nb-0.5). Iron content coefficient (FeO/MnO) varies significantly (non-manganese up to 8.6), at the same time late non-manganese varieties are often enriched in REE, U, or Y. Despite the similar patterns of chemical evolution defined for granitoid melts, the differences in U, Pb, Y, F, W, Sn, LREE, Th contents observed in tantalum-niobates of pegmatite and amazonite granites indicate heterogeneous crust magma sources and their intrusion under different paleogeodynamic conditions.

This study was funded by the Russian Ministry of Education and Science (projects 5.3143.2011, 14.B37.21.0686, 14.B37.21.1257)

DOI:10.1180/minmag.2013.077.5.2
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A “non-CHONS” stable isotope view on weathering and hydrology

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The past 15 years have witnessed a remarkable expansion in our knowledge of “non-CHONS” stable isotope systems (that is, stable isotope systems other than Carbon, Hydrogen, Oxygen, Nitrogen or Sulfur). The metals and metalloids studied thus far having demonstrated isotopic variability span the periodic table, vary from major to trace element abundances in natural materials and have a broad range of geochemical affinities and behaviors. Highly precise stable isotope measurements for these elements are currently obtainable using multi-collector ICPMS, TIMS and SIMS instruments, potentially allowing efforts at cross-platform validation of data accuracy. In surveying the rapidly building literature on the topic, it is becoming increasingly clear that we have spent as much effort determining why the “non-CHONS” stable isotope systems behave as they do in our laboratory and field-based experiments (e.g. the focus on distinguishing equilibrium from kinetic isotope effects, biotic from inorganic controls, natural from anthropogenic signals) as we have in using the isotopes to tell us unique information about the systems we are studying. Now that we have gained a broad understanding of isotope fractionation mechanisms and their implications for natural isotope distribution patterns for at least some of the non-CHONS stable isotope systems, the time is ripe to concentrate on demonstrating and promoting the utility of these systems for understanding Earth processes such as physical and chemical weathering and their intricate linkage to hydrology. In the broad realm of weathering and hydrology research, the greatest attention has been directed to the Li, B, Mg, Ca, Fe and Si stable isotope systems and each seems to have found one or more particular testable niches (e.g., Li isotopes to distinguish silicate from carbonate weathering, Ca isotopes to discern biotic influences on global flux calculations, Fe isotopes as a (paleo)redox proxy and potential biosignature). More recently, additional redox proxies such as U, Ti and Cr stable isotopes and tracers of biological processing such as Sr and Ba stable isotopes have been explored. This presentation will highlight some new directions for linked weathering/hydrology research in which the non-CHONS stable isotope systems can play a key role, as well as some of the challenges remaining as we move these stable isotope systems from “non-traditional” to the mainstream.

The societal impact of urban and environmental geochemistry: Pathways to success

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Taken together, the fields of urban and environmental geochemistry represent a relatively new, broad and important branch of geochemical research. Given the obvious, that urban and environmental geochemistry focuses on where people live, it could be expected that ever-expanding scientific endeavors in this field would have considerable impact on policy, regulatory decision making and public perception of the importance of sound science. There are many examples of “success stories”, where sound science and persuasive communication has resulted in changes in the way we do business as a society (e.g. implementing limits on stack emissions in response to the effects of acid rain, regulating sulfate loading in the Everglades to limit methylation of mercury, encouraging green space in urban areas to lessen impacts of hydrologic rerouting). On the other hand, the ongoing debate over the validity of climate change science as a driver of policy implementation reveals that scientists are not always the best communicators when forced to defend their science to non-scientists. Because science is complicated and has a language all its own that can be difficult for non-scientists to grasp, it is important that research results having policy implications be carefully communicated to the people charged with making and implementing policy. In this regard, the scientific logic and approach must be beyond question and implemented without bias toward a particular position or outcome. However, possible outcomes should be anticipated and potential solutions considered. Results need to be communicated at an understandable level, keeping the message on target but as simple as possible. And scientists need to stand their ground, letting the science speak for itself. Perhaps most importantly, we need to make sure that policy experts are invited to participate in our scientific conferences and workshops and to make presentations outlining their needs and perspectives, thus allowing the conversation to begin early in the process of developing regulatory policy. This presentation will showcase a collection of success stories in which urban and environmental geochemical research has influenced policy at the local, national and international level, and will attempt to identify the underlying pathways to that success.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
The structure and emplacement of the Rocche Rosse obsidian lava flow, Lipari, Aeolian Islands, Italy

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Satellite image analysis and field-based, structural mapping of the Rocche Rosse obsidian lava flow, Lipari (Aeolian Islands, Italy) provide important constraints on silicic lava flow emplacement and deformation.

High resolution satellite imagery of the flow surface identifies large scale structures, such as two well-developed flow lobes, pronounced lineaments which are prevalent along the extent of the flow, and prominent crescent-shaped ridges (ogives), typically 20-80 m in length, spaced 10-15 m apart and parallel to flow-frontal margins. Structural features measured include a pervasive foliation (flow banding), small-scale folding and flow ramps. Small-scale folding is superimposed on larger scale folding (parasitic folds), and recumbent folding is also apparent. In general, data on the ground match with structures inferred from the satellite image. Foliation and lineation orientation patterns vary across the flow, generally showing a flow parallel and flow perpendicular arrangement. A prevailing stretching lineation follows the large-scale lineament features, and surface folding is traceable along the surface ridges identified by the satellite image.

It is proposed that the structural features outlined formed over a progressive series of flow emplacement and deformation, from initial extrusion, constrictional and compressional forces, polyphase folding, brittle deformation and devitrification in the solid state. Variations in structural trends relate to areas of complex and progressive deformation. The Rocche Rosse lava flow is emplaced endogenously as a continuous, composite lava flow, with two flow lobes (formed as the advancing flow divided).

We show that while structures associated with obsidian lava flows are remarkably complex, they are inherently related and form sequentially during continuous effusion, preserve evidence for progressive deformation, and can be used to decipher mechanisms of obsidian flow emplacement, in unprecedented detail.

Setschenow constants for prediction of salting-out of petroleum hydrocarbons in brines

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Large scale implementation of carbon capture, utilization, and storage (CCUS), as well as the management of produced water associated with energy production activities (including extraction of natural gas from shale plays) requires a better understanding of the interaction of petroleum hydrocarbons with highly concentrated brines. It is not well known how very high levels of electrolytes influence the solubility of hydrocarbons. The objective of this study is to determine if existing salting-out parameters, called Setschenow constants, are applicable to predict the decrease in aqueous solubility of petroleum hydrocarbons, including polycyclic aromatics hydrocarbons (PAHs), phenols, and thiophenes, due to high levels of electrolytes in concentrated oilfield brines.

We measured the solubility of important organic compounds found in oilfield brines, such as naphthalene. Electrolytes studied include NaCl and CaCl2, which are the most common salts found in oilfield brines ([1]). The organic compounds in the brines were extracted with a 100 μm polydimethylsiloxane (PDMS) fiber using solid phase microextraction (SPME) and analyzed by an Agilent 6890 gas chromatograph coupled with a flame ionization detector (GC-FID).

We hypothesize that existing Setschenow constants measured at lower ionic strengths (e.g. up to seawater) will also predict the salting-out effect at very high ionic strengths expected in brines (5M) for a range of compound classes of interest. These results are expected to have implications for enhanced oil recovery, CCUS, and any other industry that deals with produced waters. If valid, the solubility of these compounds can be readily modeled using existing Setschenow constants determined at lower ionic strengths.

New sedimentary $^{231}$Pa/$^{230}$Th records from the northern Brazilian margin over MIS3

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The region of the North Eastern Brazilian margin is of major interest in the study of the variability of the oceanic circulation because of the large part of the Atlantic Meridional Overturning Circulation passing through it. Moreover this region has been extensively studied leading to a good chronostratigraphical framework of its marine sediment cores [1, 2, 3]

In order to better understand the changes in the AMOC during Heinrich events, we chose to study two sediment cores at different water depths so that we may observe not only changes in the intensity of circulation of the water masses influencing the cores, but as well changes in the vertical extent of these water masses.

Due to the difference in particle reactivity of $^{231}$Pa and $^{230}$Th in the water column sedimentary $^{231}$Pa/$^{230}$Th (Pa/Th) may be used to record changes in AMOC [4, 5], although particle scavenging may bias the signal in certain cases. In the case of the western equatorial Atlantic region, the sedimentary Pa/Th vertical profile measured on recent sediment is consistent with a dominant role of the AMOC, rather than particle scavenging, thereby demonstrating that Pa/Th can indeed be used to monitor changes in water mass overturning rates in that region [6].

We present new Pa/Th records from the last glacial and in particular from periods of rapid circulation changes associated with Heinrich events. Our results show that the Pa/Th ratio changed along with other proxies such as the benthic foraminifer carbon isotopic ratio.


Halogen abundances of the martian mantle

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The surface of Mars is relatively halogen-rich, with a mean Cl concentration of 0.49wt% [1]. In contrast, little is known about the martian interior halogen composition, nor how it compares with the Earth's mantle, where subduction recycling of halogens occurs. Insights into the halogen composition of the martian interior can be gained from shergottite meteorites, whose parental magmas were formed by partial melting of the martian mantle. North West Africa (NWA) 6234 is an olivine phryic shergottite [2], it is unweathered [2] and relatively undegassed, having likely crystallised at depth within the martian upper crust [3]. We analysed bulk and mineral separates of NWA6234 to determine Cl, Br and I by extension of the $^{40}$Ar-$^{39}$Ar technique. In-vacuo crushing experiments released only 2-10% of total halogens indicating that the major fraction is located within solid phases (melt inclusions or phosphate minerals). Stepped heating yielded constant molar Br/Cl = 0.0040 ± 0.0004 and I/Cl = 0.000358 ± 0.000046 throughout the release, indicative of a single halogen-bearing component. With the total Cl released (59 ppm), and assuming the basalt formed by 10-20% partial melting of the source, this implies a martian mantle Cl composition that is very similar to the terrestrial MORB source (4 ppm Cl [4]) and in agreement with a recent finding based on apatite chemistry [3]. However, NWA 6234 Br (560 ppb) and I (110 ppb) concentrations indicate a mantle enrichment of between 4-8 times and 30-70 times respectively relative to MORB. Thus, the martian interior is either less degassed of its heavy halogens compared to the Earth, or it formed with higher abundances.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Constraining the modern riverine sulfur isotopic budget

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The sulfur cycle has an important influence on global climate, for instance through weathering and aerosols, and is intricately linked to both the carbon and oxygen cycles. However, many aspects of the modern sulfur budget are not well understood. We present new 34S and 33S measurements on aqueous sulfate from more than 50 rivers from different geographical and climatic regions. These data were measured by a new MC-ICP-MS method that requires only 5 nmol of sulfate [1], with typical isotopic uncertainties of only 0.1‰. Combined with previously published sulfur isotope data, more than 44% of the world's freshwater flux to the ocean is involved in this estimate of the global riverine sulfur isotopic budget. We find a large range in the 34S of rivers, both temporally and spatially. Riverine 34S values range from -2‰ to 14‰, and some smaller tributaries lie outside of this range. Time series data from the Fraser River show a seasonal cycle in the 34S of more than 3‰.

Combined with major anion and cation data, the sulfur isotope data allows us to tease apart the relative contributions of different processes to the modern sulfur budget, including the oxidative weathering of pyrites, the weathering of sedimentary sulfates, and anthropogenic influences. These data yield important insights into the modern sulfur cycle and the weathering of sulfur bearing minerals, and are first order terms in balancing the modern sulfur isotopic budget. The large range of sulfur isotopic ratios in modern rivers also has implications for our interpretation of the past changes in the sulfur isotopic composition of seawater. Secular changes in the lithologies exposed to weathering through time could play a major role in driving the variations in 34S in seawater over the Phanerozoic.

The redox state of diamond-forming fluids: Constraints from Fe$^{3+}$/Fe$^{2+}$ of garnets
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Inclusions in diamonds afford unique glimpses of deep lithospheric and asthenospheric minerals, allowing the thermal and chemical state of the mantle to be characterised. In the host diamonds, the concentration of N, $^{15}$N/$^{14}$N and $^{13}$C/$^{12}$C all give information about the origin of fluids in the mantle. The speciation in these fluids is uncertain in many cases, with considerable debate as to whether CH$_4$ or CO$_2$ is the predominant component in the transport of C [1,2]. As methane and carbon dioxide (or carbonate) represent reduced and oxidised C respectively, this redox signature should also be reflected in other mantle minerals.

Redox conditions of diamond-forming regions in the mantle can be found from the Fe$^{3+}$/Fe$^{2+}$ ratio of garnets as determined by X-ray absorption near edge structure (XANES) spectroscopy [3]. We present Fe$^{3+}$/Fe$^{2+}$ data for several suites of diamonds: Argyle, Western Australia; Juina, Brazil; Diavik, Canada; Udachnaya, Russia; Murowa, Zimbabwe. For the first three sets of diamonds, both eclogitic and peridotitic garnets were analysed, allowing the two distinct diamond-forming events to be contrasted.

For suites in which olivine and orthopyroxene coexist with garnet, the $f$O$_2$ of the diamondiferous paragenesis was calculated following [2].

Our work aims to couple the $f$O$_2$ information obtained from garnets to trace element data and (for the eclogitic samples) their oxygen isotope ratios, allowing the geochemical evolution of the slab during subduction to be robustly constrained.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org

Patterning in stress: A new insight into the development of phase separation in metamorphic rocks
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The development of slaty cleavage, foliation and compositional banding in metamorphic rocks is understood to result from mass transport by either dissolution or diffusion under the influence of a non-hydrostatic stress field. Explanations for how compositional differentiation initiates generally rely on high shear strains to orient pre-existing features or folding of a pre-existing foliation to form a pattern of fold noses and limbs that lead to preferential dissolution. Based on 2D plane-strain finite element models, I propose a new low-strain mechanism for the formation of compositional banding based on mass transport between local regions experiencing varying levels of differential stress caused by the variations in the single crystal elastic properties of the constituent minerals in the rock. Models were constructed of 2574 hexagonal grains each containing 48 elements. Grains were assigned elastic properties appropriate for crystals of quartz, feldspar and mica in a variety of crystallographic orientations. Compression results in local variations in the differential stress that are ~ 30% of the total load and a pattern of minimum stresses that mimics foliation. This pattern could serve as a template for mass transport of the most mobile chemical components leading to phase separation.

Figure 1: Model is shortened by 0.2% vertically. The size of grains in each view is given by the yellow hexagons. Compression is negative.
**Coupling of arsenic mobility to microbial sulfate reduction in subsurface environments**

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Arsenic mobilisation is an important concern in many subsurface soil, sediment and groundwater systems. In such systems, microbial sulfate reduction often dominates anaerobic electron flow, thereby leading to the production of aqueous sulfide and the formation of iron sulfide species. However, the effects of microbial sulfate reduction on arsenic mobility in subsurface environments is poorly constrained.

This presentation describes some of our recent discoveries illustrating how arsenic mobility is coupled to subsurface sulfur biogeochemistry, especially to the production of sulfide via microbial sulfate reduction.

Our approach has been to conduct a series of integrated studies on this topic, including (i) abiotic mono-mineralogical batch experiments\(^1\), (ii) advective-flow column experiments\(^2\) and (iii) anoxic incubation experiments with complex arsenic-contaminated floodplain soil.

The results show that microbial sulfate reduction can have contradictory consequences for arsenic; either substantially retarding or greatly enhancing arsenic mobility. These vastly divergent outcomes depend on multiple factors, including hydrological flow conditions, the presence or absence of elevated porewater sulfide concentrations, aqueous arsenic concentrations and reaction time.

The fact that sulfate reduction can both retard or enhance arsenic mobility, depending on environmental conditions, represents a serious challenge for managing arsenic-contaminated systems. In particular, it implies that great caution must be exercised when aiming to exploit natural sulfur biogeochemistry as a strategy for mitigating arsenic mobility in subsurface environments.


**Unradiogenic lead in the mantle source of Mid-Ocean Ridge Basalts**

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The isotope composition of lead (Pb) in the silicate Earth appears to be far too radiogenic for evolution from chondritic (primitive solar system) material over 4.57 billion years, the so-called ‘Pb paradox’. Loss of Pb to the core, storage in the lower continental crust, or arrival in a late veneer, have all been proposed as mechanisms to account for this imbalance, but each remains problematic. Recently is has been suggested that the upper mantle itself, could serve as a complementary reservoir of unradiogenic Pb, sourced in either sulphide \(^1\) or silicate minerals \(^2\), but it remains unclear why such material is not sampled by oceanic basalts.

This study presents high-precision double-spike Pb isotope data for the constituent phases of Mid-Ocean Ridge Basalts (glass, plagioclase and sulphide) from a single ridge segment from the FAMOUS region (36°50’N) on the Mid-Atlantic ridge. Separated phases from individual samples show a remarkable variation in Pb isotope composition, greater than that seen for all basalts previously analysed from this ridge segment. These variations cannot be explained by assimilation of seawater altered oceanic crust or by contamination from the Azores hotspot, both of which carry a radiogenic Pb isotope signature. Rather they indicate mixing between an early extremely unradiogenic melt, from which plagioclase crystallised, sourced by mantle material showing long-term depletion of U, and a later more radiogenic melt sampled by the glass. Elemental data suggest that the mantle source of this early melt was small-degree, water-rich with a garnet-like signature.

The fact that sulfate reduction can both retard or enhance arsenic mobility, depending on environmental conditions, represents a serious challenge for managing arsenic-contaminated systems. In particular, it implies that great caution must be exercised when aiming to exploit natural sulfur biogeochemistry as a strategy for mitigating arsenic mobility in subsurface environments.

Reconciling ground deformation and degassing activity at Mt. Etna

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Etna exhibited both steady inflation and persistent degassing between 1993 and early 2001. The source volume increase associated with the inflation was deduced using a Mogi model to fit the observed deformation pattern. The mass of SO\textsubscript{2} released in the same period was produced by degassing magma. With knowledge of the original S concentration dissolved in the parental magma it is possible to determine a minimum mass of magma consistent with the observed gas emissions. This mass of degassed magma is more than two orders of magnitude larger than the mass of erupted magma in the same period, implying that the degassed magma was endogenously stored within the volcano. We wish to test the hypothesis that this stored degassed magma was responsible for the observed inflation of the edifice.

An initial comparison of the volume of degassed magma compared with the change in volume associated with the ground deformation reveals that the former is 4 times greater than the latter, suggesting that our hypothesis is incorrect. However, when a combination of magma compression and viscoelastic deformation of hot crustal material heated is taken into account, the deformation source volume changes can, instead, be successfully reconciled with the volume of degassed magma.

Thus, it appears we cannot exclude the hypothesis that during the observation period ground deformation at Etna was controlled by permanent storage of degassed magma in the plutonic zone 5-8 km beneath the surface. In this manner, the constant magma supply indicated by the persistent degassing of the volcano produces a quiescent accumulation of degassed magma at the roots of the volcano, slowly pressurizing and inflating the edifice.

A global volcanic CO\textsubscript{2} flux inventory

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CO\textsubscript{2} degassing from the Earth has played a fundamental role in controlling climate through a series of feedback mechanisms including CO\textsubscript{2} removal through weathering in proportion to the magnitude of greenhouse warming produced by CO\textsubscript{2} in the atmosphere. Constraining CO\textsubscript{2} emission rates from volcanic sources would allow an improved understanding of the relative magnitude of natural and anthropogenic outputs today, shed light on the role of volcanic emissions in the pre-industrial climate and improve our knowledge of carbon recycling though the mantle.

Notwithstanding this, the flux of CO\textsubscript{2} from the Earth remains poorly quantified. The uncertainty in our knowledge of this critical input into the geological carbon cycle led Berner and Lugasa (1989) to state that it is the most vexing problem facing us in understanding that cycle.

To date, CO\textsubscript{2} fluxes have been directly measured on approximately 23% of the world’s actively degassing subaerial volcanoes. Here we present an updated assessment of the global volcanic CO\textsubscript{2} flux, based on these empirical observations. We use this inventory to extrapolate to an estimate of global volcanic CO\textsubscript{2} emissions, and to investigate rates of carbon recycling through the mantle.
Disequilibrium melting recorded in isotopic and trace element compositions of a pulsed granitoid, Mt Kinabalu, Borneo

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Geochemical heterogeneity in silicic systems - and by implication heterogeneities in the continental crust - can be derived from the melting processes or variations in their deep source regions. Mixing and assimilation during the ascent and emplacement of silicic plutons are also invoked to explain observed heterogeneities. We present a range of geochemical data collected from the zoned granite and granodiorite pluton of Mt Kinabalu in NW Borneo to provide insight into the role of such processes in development of this body and the timescales over which they occur.

The Mt Kinabalu pluton is an isolated post-orogenic intrusion. It formed following the Miocene orogenic inversion event recorded in NW Borneo that emplaced attenuated S. China crust, similar to the attenuated Mesozoic tonalitic crust of the South China Sea, beneath the region’s ophiolitic basement. Post-orogenic extension and rapid related uplift (aided by the fast erosion rates of the region) led to dehydration partial melting of the tonalitic crust.

Melting resulted in the emplacement of five petrographically distinct major units at ~0.2Ma intervals, the first four between 7.85 and 7.22Ma (U-Pb in zircon, [1]). The oldest unit possesses significantly more radiogenic Sr and Pb and less radiogenic Nd isotope ratios than later units. This could be interpreted as evidence for isolated derivation or mixing of multiple sources, or contamination of one source. However, there is no accompanying variation in δ¹⁸O or trace element ratios. More substantial trace element variation is displayed between the later units that display little isotopic contrast with one another. Instead, we interpret the isotopic data and trace element variations as the result of progressive disequilibrium melting under increasingly warmer conditions of the same region of relatively homogeneous crustal source rocks.


Transport of carbon colloid supported nano zero-valent iron

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Nano zero-valent iron (nZVI) is an emerging technology for in situ groundwater remediation. Due to its high reactivity, nZVI is able to dechlorinate organic contaminants and render them harmless. Carbo-Iron is a newly developed composite material consisting of activated carbon colloids (d₅₀ = 0.6-2.4 µm) that are doted with nZVI particles. These particles combine the sorption capacity and mobility of activated carbon colloids and the reactivity of nZVI. Results from column tests and a two dimensional laboratory aquifer test system are presented: Column tests using columns of 40 cm length were filled with porous media. A particle suspension was pumped through the system. Results show, addition of a polyanionic stabilizer such as Carboxymethylcellulose (CMC) is required to enhance mobility. Ionic strength and pH concentrations in an environmental relevant range do not interfere significantly with transport, but particle size was found to be crucial. Another experiment was performed in a two dimensional aquifer test system. The test system contains a sand filled container with an inner size of 40 x 5 x 110 cm and seven ports on each side. A constant flow of water was applied from the left to the right side through all ports and the middle port was fed with a Carbo-Iron suspension. Results show transport through the laboratory aquifer within few exchanged pore volumes, and breakthrough of ~60% of the injected concentration of Carbo-Iron at the outlet. Deposits of immobile Carbo-Iron were found to be decreasing with distance from the injection port. No gravity effects were observed. Results suggest high mobility of carbon supported nZVI under environmental relevant conditions. Carbo-Iron might be helpful to deliver nZVI into contaminated aquifers. Here 1D and 2D results support the design of a field test and application of Carbo-Iron for nZVI delivery.
**Delta $^{34}$S of discrete authigenic framboidal pyrite: A powerful palaeo-indicator for barrier estuary closure**

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This study relates microscale isotopic variability of discrete authigenic framboidal pyrite to the palaeo-depositional conditions of a barrier-estaury on the east coast of Australia. Light sulfur isotope ($^{32}$S) is preferentially utilised in microbially mediated pyrite formation, with the extent of fractionation dependent on how ‘open’, or ‘closed’, the depositional environment is to a replenishing supply of sulfate. An open system has an unlimited supply of the preferred, light sulfate during sedimentation. In a closed system, all of the sulfate, light and heavy (i.e.$^{34}$S), is eventually utilised.

Intact sediment cores were collected from the lower Richmond River floodplain. Sampling encompassed the last 6000 years of sedimentation, extending to a depth of 5m. The isotope composition of discrete pyrite framboids was determined on select layers using secondary ion mass spectrometry[1]. The striking result was an anomalous enrichment of $^{34}$S in pyrite at 1.7–2.5m depth, with $^{34}$S peaking at +50%o (-20 to +10%o is the normal range for estuarine sediments). The microscale isotopic variability between pyrite framboids in this layer had a broad distribution, consistent with that theoretically predicted by Seal and Wandless[1], for a ‘closed’ system. This study provides the first demonstration of microscale sulfur isotope frequency distribution as a tool for identifying in the sediment record, periods of closure of barrier estuaries or other coastal embayments to marine influences.


**Nitrogen cycle in the late Archean ferruginous ocean**

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The Hamersley Group comprises a Late Archean sedimentary succession, which is thought to record the prelude to the atmospheric oxygenation in the early Paleoproterozoic, the so-called Great Oxidation Event (GOE) dated at around 2.4 Ga. In the present work, drill-core samples of sedimentary rocks from the upper Mount McRae Shale and Brockman Iron Formation deposited before the GOE at ~2.5 Ga were examined in order to characterize the environments and ecosystems prevailing during their deposition. We analyzed the concentration and isotopic composition of C in carbonate and organic matter, bulk N content and its isotopic composition, and major element concentrations.

The $^{13}$C$_{\text{carb}}$ values, ranging from -10.7 to -3.2 ‰, reflect diagenetic carbonate precipitation, with markedly negative values representing Fe-rich carbonates formed via organic matter mineralization with ferric oxyhydroxides. In contrast, $^{13}$C$_{\text{org}}$ and $^{15}$N values record primary isotope signatures derived from ancient living organisms. The near constant $^{13}$C$_{\text{org}}$ values at -28.7 ± 0.8 ‰ are interpreted as reflecting photoautotrophs thriving on a large pool of dissolved inorganic carbon. Whole-rock N analyses show highly variable concentration, between 1.3 and 785 ppm, and $^{15}$N values range between 0.4 and 13.4 ‰. Inverse relationship between $^{15}$N and $^{13}$C$_{\text{carb}}$ values characterize the Brockman Iron Formation. We propose that N and C biogeochemical cycles were connected via Fe redox processing in the water column and in sediments of the Late Archean ocean. Several models coupling N and Fe biogeochemical cycles are considered involving different redox states of the water column. Similar positive $^{15}$N values might record very different N biogeochemical cycles under fully anoxic, redox-stratified, and oxic conditions of the ocean. Interpretation of N isotopes in terms of N biogeochemical cycle thus requires independent constraints on the redox structure of the ocean.

**DOI:** 10.1180/minmag.2013.077.5.2

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Relating grain-scale weathering observations to catchment-scale critical zone morphology

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It is well known that chemical weathering and porosity development in rocks are coupled. It is less understood how these coupled processes, which operate at the mineral grain-scale, impact larger-scale phenomena such as watershed fluxes and regolith and landscape development. The Bisley watershed in the Luquillo Critical Zone Observatory (Puerto Rico) is formed on meta-volcaniclastic bedrock that is blanketed by thick regolith comprised of thin soil overlying saprolite embedded with corestones. Saprolites here are highly leached; as a result, most chemical weathering fluxes are attributed to weathering at the bedrock-saprolite interface. However, corestone surfaces and fractures represent multiple “bedrock-saprolite interfaces” distributed throughout the regolith profile. Here we compare macro-scale weathering profiles (m’s thick) in saprolite to micro-scale (mm’s thick) profiles across corestone weathering rinds. Buried corestones were sampled by drilling two boreholes (27 and 37 m deep).

Weathering fronts are most dramatic in rinds on corestone fractures and surfaces. For example, ~40% of the protolith Mg is lost over ~3 mm of rind. In saprolite hand-augered to a corestone at 9.3 m, the final 20% of protolith Mg is lost over ~8 m. These fronts may reflect different weathering mechanisms as well as different weathering rates.

Pyrite crystals, which are of low abundance in these rocks and not detected by powder XRD, were identified by SEM in many of the thin sections and appear to be the first mineral to weather. In thin sections containing fracture surfaces, pyrite is present in many of the thin sections and appear to be the first mineral to weather. In thin sections containing fracture surfaces, pyrite is present in multiple “bedrock-saprolite interfaces” distributed throughout the regolith profile. Here we compare macro-scale weathering profiles (m’s thick) in saprolite to micro-scale (mm’s thick) profiles across corestone weathering rinds. Buried corestones were sampled by drilling two boreholes (27 and 37 m deep).

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Pyrite crystals, which are of low abundance in these rocks and not detected by powder XRD, were identified by SEM in many of the thin sections and appear to be the first mineral to weather. In thin sections containing fracture surfaces, pyrite is associated with increased porosity and dissolving plagioclase and amphibole grains. These associations are observed even cm’s inboard of the visible weathering rinds. Although present only in trace amounts, pyrite appears to play a controlling role in secondary porosity development and weathering of the major minerals by releasing sulfate during oxidative dissolution, creating micro-environments of highly reactive, low pH fluid within the corestones. Where the bedrock contains more pyrite, corestones may split and shrink more readily, affecting mineral weathering rates and larger-scale phenomena such as the size and distribution of corestones within the regolith profile.

Organic geothermometry: Defining metamorphic grades in coal

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Mechanical and chemical variations created during metamorphism of organic compounds is an overlooked subject. The fundamentally structure of organic materials is analogous to that of inorganic materials such as minerals and rocks, but the organic equivalents are subject to generalities of both structure and chemistry which has left the interpretation of the metamorphic products of these materials vague and unspecific. The physiochemical nature of the coal and its macerals is currently quantified using thermogravimetric proximate analysis, which aims define the properties of coal through the quantification of moisture %, ash%, volatile% and calorific value.

A new approach was used to analyse the physiochemical character of the coal in close proximity to a dolerite intrusion on both macro and micro scales. Macro scale structural analysis has been done through the use of a Schmidt hammer to quantify in situ physical variation within the coal. In conjunction, conventional proximate analysis was employed to estimate the “chemical” variations within the coal. It was expected that the fundamental link between chemical properties and physical character would be displayed in the resultant analysis, but no direct link between the proximate analysis and Schmidt hammer results was observed, either as a result of inherent heterogeneity of coal or a display of the short comings of the proximate analysis method. In light of these results, a new approach was applied by using pressurized liquid extraction (PLE) combine with two dimensional gas chromatography time of flight mass spectrometry (GC*GCTOFMS) to produce detailed chromatograms of the organic constituents of the coal. The technique will allow quantification of the organic components within the coal. Due to the variable sensitivity of organic compounds to fluids, salinity, pressure and temperature, it may be possible to define not only the temperature of metamorphism but also the type i.e. metasomatic or contact and also the salinity of the metamorphic fluid.
Characterization of a novel multicopper oxidase that oxidizes Mn(II)

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Manganese (Mn) oxides are some of the most reactive mineral phases in the environment and control the distribution and bioavailability of a variety of toxic and essential elements. Mn oxide minerals are believed to be formed either directly or indirectly through the activities of microorganisms. The ability to oxidize Mn in several phylogenetically distinct groups of bacteria has been attributed to enzymatic oxidation by a multicopper oxidase (MCO), a family of proteins that utilize multicopper atoms in catalytic sites to oxidize their substrates, typically Fe(II) or phenolic compounds, in one electron reactions. Here we report the expression, purification and partial characterization of a Mn-oxidizing MCO and preliminary efforts to reconcile the one-electron chemistry of MCOs with the two-electron oxidation of Mn(II) to Mn(IV) oxide.

Many attempts have been made to purify the suspected Mn-oxidizing MCO from a variety of different bacteria, including species of Pseudomonas, Leptothrix, Pedomicrobium and Bacillus. In many species of marine Bacillus it is the mature spores that oxidize Mn(II). Oxidation occurs on their exosporium, the outermost layer of the spore, encrusting them with Mn(IV) oxides. Previous studies identified the mnx genes, including mnxG, a putative multicopper oxidase, as responsible for the two-electron oxidation of Mn(II). Its characterization, however, has been hampered by the difficulty in obtaining purified protein. By purifying active protein from the mnxDEFG expression construct, we found that the resulting enzyme is a blue (Abs max 590nm) complex containing MnxE, MnxF, and MnxG proteins. The complex oxidizes both Mn(II) to Mn(III) and Mn(III) to Mn(IV) resulting in the formation of a Mn(IV) oxide mineral. X-ray absorption spectroscopy of the Mn mineral product confirmed its similarity to Mn(IV) oxides generated by whole spores or purified exosporium. With the purification of active Mn oxidase, we will be able to unravel the mechanism of Mn oxidation and broaden our understanding of Mn oxide mineral formation and the bioinorganic capabilities of MCOs.

Inventing the Phanerozoic biological pump - and inducing Snowball Earth

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Export production in the modern oceans is dominated by relatively large/biominalerizing eukaryotic phytoplankton, often accelerated by animal-mediated repackaging in the form of fecal pellets, appendicularian houses and carcasses. Prior to the evolution of animals, and the co-evolutionary radiation of photosynthetic eukaryotes, the biological pump would have worked in a fundamentally different fashion. The transition between these two alternate states appears to have begun in the mid-Neoproterozoic (Tonian/Cryogenian), and achieved a recognizably Phanerozoic condition in the early (but not earliest) Cambrian.

Modern aquatic ecosystems exhibit marked hysteresis between clear-water eukaryote-dominated conditions and an alternative turbid-water cyanobacterial state, typically mediated by suspension-feeding metazoans. In marine shelf environments, the particular ability of sponges to draw down turbidity-inducing DOC, and actively select for larger more export-prone phytoplankton, imparts a first-order control on the biological pump. This in turn presents the circumstances for a more general exploitation of the water column by eumetazoans, especially bilaterians, leading to multi-trophic food-webs, enhanced ventilation and complex feedback effects on nutrient cycling and export.

Biomarker evidence suggests that Proterozoic export was dominated by cyanobacteria. The first quantitatively significant occurrence of eukaryotic steranes appears shortly before the Cryogenian glaciations, along with a novel suite of eukaryotic microfossils. Although there is no direct fossil record of animals at this time, there is a case for recognizing these changes as a co-evolutionary consequence of newly introduced animal activity. Intriguingly, current molecular clock analyses place the first appearance of simple (sponge-grade) animals in this same mid-Neoproterozoic time-frame.

Changes to the mid-Neoproterozoic biological pump are likely to have induced major increases in oceanic alkalinity, leading to a draw-down of atmospheric CO2 and potentially triggering Cryogenian glaciation [1]. As such, the pronounced evolutionary, biogeochemical and climatic perturbations of the terminal Proterozoic may all be causally linked to the evolutionary appearance of animals.

Experimental study on interaction of the H2O-NaCl fluid and model peridotite at 6 GPa

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In order to study the effect of NaCl on the Al2O3, CaO, Na2O-rich H2O-bearing peridotite transformation at pressures above 3 GPa, we have conducted the experiments on interaction of model peridotite $\text{Fo}_{57}\text{En}_{17}\text{Prp}_{14}\text{Di}_{12}$ with the H2O-NaCl fluid at 6 GPa and 1050-1450°C. Starting materials were mixtures of oxides, Mg(OH)2 and jadeite (mg): SiO2 (37.04); Al2O3 (3.66); CaO (3.62); Mg(OH)2 (48.30); MgO (4.14), NaAlSi2O6 (3.24). NaCl added at 8 wt. %, that corresponds to mole fraction of $X_{\text{NaCl}} = \text{NaCl}/(\text{NaCl}+\text{H2O})$ in the fluid 0.05. The present experiments were performed using Pt capsules of 0.02 mm of the wall thickness.

In absence of NaCl in the fluid, the assemblage $\text{Fo+Opx+Cpx+Grt}$ was observed in the solidus of the model peridotite, while melting began at about 1200-1300°C. Clinopyroxene shows the increase of jadeite content with increasing temperature. Addition of NaCl reduces melting temperature down to 1050-1100°C. Amount of orthopyroxene and garnet in solids decreases, the Al content in orthopyroxene decreases, and the jadeite content of clinopyroxene increases in presence of NaCl. These relationships can be described by the following reactions:

1. $\frac{1}{4}\text{Mg-Ts} + \frac{7}{4}\text{En} + \frac{1}{2}\text{NaCl} + \frac{1}{2}\text{H2O} = \text{Fo} + \frac{1}{2}\text{Jd} + \frac{1}{2}\text{HCl}$
2. $\frac{1}{4}\text{Prp} + \frac{5}{4}\text{En} + \frac{1}{2}\text{NaCl} + \frac{1}{2}\text{H2O} = \text{Fo} + \frac{1}{2}\text{Jd} + \frac{1}{2}\text{HCl}$
3. $\frac{1}{4}\text{Grs} + \frac{11}{4}\text{En} + \frac{1}{2}\text{NaCl} + \frac{1}{4}\text{H2O} = \text{Fo} + \frac{3}{4}\text{Di} + \frac{1}{2}\text{Jd} + \frac{1}{2}\text{HCl}$

(where Mg-Ts – Mg-Tschermack molecule, MgAl2SiO6 in orthopyroxene, En – enstatite, Fo – forsterite, Prp – pyrope, Grs – grossular, Di – diopside, Jd – jadeite). These reactions show the destabilization of Grt-Opx association in the presence of NaCl fluid.

Thus, addition NaCl in the H2O-peridotite system does not influence on phase assemblages. However, changing of mineral compositions, mostly increase of the jadeite content in clinopyroxene, results in the decrease of melting temperature. Present experiments further support our conclusion [1] that the effect of interaction of alkali chlorides with silicates in complex peridotite assemblages overpowers the effect of the reduced H2O activity in the brine fluid [2].


Pyroxene megacrysts in anorthosites: Revealing continental crust-forming processes at Moho depths

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The mismatch between bulk, intermediate compositions (SiO2 > 60 %) of the continental crust and predicted basaltic compositions (SiO2 < 50 %) of mantle-derived melts in crust-forming environments poses a major problem in models of crustal evolution and requires that a mafic component be physically separated from felsic end-members. Although information from the Moho, where some of these poorly understood crustal differentiation processes are thought to occur, is rare, giant (up to 1 m in length), high-pressure (30-40 km) pyroxene megacrysts and comagmatic Proterozoic anorthosite massifs provide insight into crust-mantle differentiation processes at these depths. Using Nd and Pb isotopes, we provide direct evidence for megacyrst crystallization in isotopically homogenous magmas that ponded at the Moho (Figure 1). These megacyrsts are 110-130 m.y. older than the comagmatic anorthosites that host them, indicating that the magmatic system is long-lived. In combination with EC-AFC modeling, these data also indicate that Proterozoic anorthosites are derived from melting of the depleted mantle at long-lived Andean-type margins. This evidence for ultramafic cumulate formation illustrates that fractionation of ponded magmas at the Moho is a significant mechanism in crustal differentiation and that the loss of these dense phases to the deeper mantle may represent an important component of crustal recycling.

Figure 1: Isochronous high-pressure megacyrsts in three Proterozoic anorthosite massifs from Canada and Norway.

DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Geochemistry of trace elements in gas phase of thermal springs

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The composition of the thermal waters studied well, but there are only few articles on the geochemistry of trace elements in thermal springs gas phase. Samples of the coexisting liquid and gas phases were collected in thermal springs of Kamchatka peninsula (Russia): Mutnovsky volcano, Uzon Caldera, Geyser Valley, Karymsky volcano. For the sampling of thermal springs specially designed installation was used, wells of Mutnovsky geothermal plant was studied by standard two-phase separator of steam-water mixture. More than 200 samples of coexisting gas and liquid was collected. In samples the concentration of major and trace elements and hydrogen and oxygen isotope composition were determined.

The distribution of high volatile elements, such as boron and arsenic in geothermal wells steam-water mixture was found close to experimental data. However gas phase condensates from thermal springs compared with the liquid phase are enriched with boron and arsenic. This cannot be explained by the equilibrium distribution of components by experimental data. This effect is observed only for thermal springs with superheated steam and correlates with the isotopic composition of the condensates. Perhaps distribution of the superheated steam is determined by the equilibrium at high temperatures in the depth of hydrothermal system. Boron concentration of the condensate can be used to detect the temperature of the gas phase separation and deep boiling. The calculations show good agreement with other geothermometric methods.

For nonvolatile elements, such as REE, Ga and others, distribution coefficients were calculated. Some correlations between the partition coefficients were shown. So, for LREE they are higher than for HREE. These coefficients can’t be calculated from thermodynamic data, since the speciation of elements in the gas sufficiently studied. New experiments of solubility in the gas phase can explain distribution coefficients, as shown by the example of gallium. For this element the gas form Ga(OH)3 was determined by gallium oxide solubility in vapor. This experimental data can explain the dependence of the distribution coefficient of the pH of thermal water.

This study was supported by RFBR 12-05-00957.

Subduction modification of Western North America lithosphere - Priming for destruction?

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Destruction of continental lithospheric mantle has been shown to be an important process that may affect the preservation of continental crust [1]. Geochemical data from mantle xenoliths indicate that the majority of the Proterozoic lithospheric mantle beneath the central Rio Grande Rift (RGR) has been convectively removed [2]. Weakening of the lithospheric mantle by addition of metasomatic fluids/melts during Laramide flat-slab subduction followed by increased mantle flow due to Farallon slab roll-back may have triggered this lithosphere destruction. If metasomatism is related to the recent deformation/destruction of the lithosphere beneath the RGR, then mantle metasomatism recorded in remnant lithospheric mantle xenoliths should also be recent.

We examined the trace element and Sr-Nd-Os-Hf isotopic composition of two suites of lithosphere-derived spinel-peridotite xenoliths from Cerro Chato (Eastern Colorado Plateau margin) and Elephant Butte (central RGR) to constrain the timing and source of mantle metasomatism. 187Os/188Os ranges from 0.114-0.126 and T 200 ages for the most depleted samples range from 1.6-2.2 Ga; similar to the age of the crust in the region [3]. Both suites of xenoliths are LREE-enriched with variable negative HFSE anomalies relative to REE. (La/Sm)N in cpx ranges from 2-14 and is correlated with 87Sr/86Sr which range from 0.7031-0.7045. εNd ranges from 4-10 and εHf ranges from 17-304. There is no correlation between 143Nd/144Nd and Sm/Nd which suggests metasomatism is recent. This is consistent with young (~250 Ma) Nd model ages for the xenoliths. A Hf pseudoschoonor (using WR Lu/Hf due to equilibration above Lu-Hf closure temperature) yields an age of ~1.0 Ga, which is younger than the Os model ages. The young Hf age may be the result of mixing and partial resetting of Hf isotopes by metasomatism as evidenced by a correlation between 1/1[HI] and 176Hf/177Hf. The most radiogenic sample has a DM-model age of 1.45 Ga which is close to the age of the overlying crust. Arc-like metasomatic signatures and young Nd model ages are consistent with metasomatism being recent and related to Farallon slab subduction. This may have primed the Colorado Plateau for deformation similar to that observed in the RGR.


DOI:10.1180/minmag.2013.077.5.2
www.minersoc.org
Microbial redox cycling of surface Fe-ions in magnetite nanoparticles

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Iron is an essential element for all microbes, with different oxidation states by some even used as an electron source or as a terminal electron acceptor. The phototrophic iron-oxidizer Rhodopseudomonas palustris TIE-1 uses energy from light and electrons from ferrous Fe(II) for growth and respiration, whilst Geobacter sulfurreducens combines the oxidation of organic compounds or hydrogen with the reduction of ferric Fe(III). Iron is almost exclusively observed to be bioavailable to the bacteria as aqueous Fe(II) or in poorly crystalline Fe(III) (oxyhydr)oxides such as ferrihydrite. More crystalline iron minerals such as magnetite or siderite are not usually considered to be biologically active. Magnetite is a mixed valent iron oxide Fe(II/III)O, which is often seen as the end member product of the microbial reduction of ferrihydrite, though very rarely as a result of microbial oxidation of Fe(II).

This study focuses on the oxidation of superparamagnetic magnetite nanoparticles (~20 nm) by strain TIE-1 and the potential mineralogical changes which result. Through in situ magnetic measurements and iron extraction methods, we found that the cells are capable of directly oxidizing the surface of magnetite nanoparticles and thereby decrease the overall magnetic susceptibility of the mineral. This effect occurs in the absence of any aqueous Fe(II) in the growth medium and only magnetite provided as the electron donor. Significantly, this process can be reversed through Fe(III) reduction by G. sulfurreducens, which in turn leads to an enhancement of the magnetic properties of the nanoparticles. Changes in magnetic properties were also detected in experiments using magnetite with varying stoichiometric ratios (i.e. Fe(II)/Fe(III)). Such effects were not observed in abiotic experiments which did not contain any bacteria.

These results demonstrate that iron ions bound at the surface of crystalline minerals such as magnetite are bioavailable for microbial respiration and can potentially be used as a source of iron in reducing or oxidizing conditions, with the potential to cycle the surface redox properties depending on the conditions present. Such modifications may provide a route towards enhancing remediation strategies that are based on the highly reactive surface of magnetite. These effects may also have implications on paleomagnetic measurements in microbially active environments.

DOI:10.1180/minmag.2013.077.5.2
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