

Effect of climate change-driven sea water intrusion on the mobilisation of Tc(VI) from reduced sub-surface sediments

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Nuclear fuel cycle operations have resulted in a significant legacy of contaminated land that requires long term management or remediation. Future sea level rise predictions suggest that nuclear facilities situated in coastal locations will become threatened in terms of seawater intrusion. Increased pore water salinity coupled with any influx of oxygenated seawater may impact on the stability of radionuclides associated with sub-surface sediments. Of particular concern is the high yield, redox sensitive fission product ⁹⁹Tc which, under reducing conditions, accumulates in sediments as hydrous Tc(IV)n.H₂O phases.

In this work Tc (1 μM) was reduced and sorbed with sediments under anaerobic conditions. Although nitrate has been reported to inhibit Tc reduction, in this study extensive sorption of Tc (87%) was observed during nitrate reduction. Tc reduction increased to 98% with the onset of Fe reduction.

Mobilisation of Tc(IV) from initially nitrate- and iron-reducing sediments into groundwater and seawater was then studied using batch and column experiments. Batch results showed that Tc was oxidised prior to mobilisation in groundwater and seawater. Limited release into degassed seawater suggested that the formation of soluble Tc(IV) carbonate or colloidal species was not significant. Release of Tc from the initially nitrate- and iron-reducing sediments into groundwater was broadly similar, with 36-48% mobilised after 90 days. In contrast, the initial redox status of the sediments had a marked effect on Tc mobilisation into seawater. Significantly less Tc was released from sediments with ingrowth of Fe(II) (17 ± 2%) compared with the nitrate-reducing sediments (45 ± 7%). These results suggest that Fe(II) phases are able to hinder Tc reoxidation and release into seawater. In column experiments a near instantaneous pulse (4-7%) of Tc was mobilised, followed by a slower sustained release that continued for the duration of the month long experiments, resulting in > 90% Tc release.

Reduced sediments may therefore act as a secondary source of Tc to marine environments during sea level rise-driven intrusion. Mobilisation occurs primarily via reoxidation whilst changes in pore water salinity alone appear unlikely to increase the rate and extent of Tc release.

Mercury and enstatite chondrite origins by equilibrium condensation from chondritic-IDP enriched vapor

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Mercury's core is at least 60% of its mass, compared to Earth's ~32%. The origin of Mercury's anomalous core and low FeO surface mineralogy [1] are outstanding questions in planetary science. If Mercury accreted primarily from a local annulus of precursor solids [2], then Mercury's composition may result from chemical controls on equilibrium partitioning of Fe and Si between those solids and coexisting vapor. High temperatures and enrichment in solid condensates or 'dust', relative to H-rich vapor, are likely conditions near the midplane of the inner solar protoplanetary disk. FeO-rich silicate liquids similar to the liquids quenched in ferromagnesian chondrules are thermodynamically stable in oxygen-rich systems that are highly enriched in a dust of CI-chondrite composition [3]. However, the solids surviving into the orbit of Mercury's accretion zone were probably more similar to FeO-poor, anhydrous, ice-free and organic-rich chondritic (interplanetary) dust particles (C-IDPs) [4]. Chemical systems enriched in C-IDP dust can produce condensates with atomic Fe/Si 50% above chondritic [5] for conservative estimates of C-IDP composition and enrichments of up to 1000x. These Fe/Si ratios approach that estimated for bulk Mercury. Stable minerals are FeO-poor, and include CaS and MgS. These reduced species are also found in enstatite chondrites. Disk gradients in volatile compositions of planetary and asteroidal precursors may at least partially explain Mercury's anomalous composition, as well as some meteorite parent body compositions. This model predicts low Ca/Al, and very low FeO content of Mercury's surface rocks.

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Geochemical and mineralogical studies on the Fe-Mn deposits of Dehbid area, Fars province, South Iran

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The Dehbid Fe-Mn deposits are located at about 260 Km of northeast of Shiraz (Fars Province), in the Sanandaj- Sirjan metamorphic zone. The deposits are hosted by shale and limestone of the Lower Devonian and thick massive limestone of the Middle and Upper Devonian. The studied area is affected by two metamorphism phases, therefore, the sequence of limestone and shale sediments in the Devonian have been transformed to garnet mica schist - amphibolites and marble.

The main ore bodies are accommodated as lenticular and vein, which are concordant to the host rock bedding. Some 5 veins have been mapped in the area; they are classified in two groups with 2-8m wide, and 20-850m long. Mineralogical studies show that the ores are including magnetite, hematite, goethite, pyrite, pyrolusite, and psilomelane. Gangue minerals include quartz and carbonate. The values of the Fe₂O₃ and MnO vary between 30 to 80 wt% and 2-13 wt%, respectively. Co/Ni ratios in the hydrothermal iron deposits are between 0.2-7 and in the Dehbid area the ratio ranges 0.1 to 3.6 that characterizes hydrothermal origin of magnetite.

Geology, petrography and sedimentology aspects indicate the Fe- Mn prospect of the Dehbid which is a strataband type deposit. Moreover, giving the influence of volcanic phase occurred in the lower Devonian and the combined geochemical evidences; the origin of the materials is considered distal Sedimentary- Exhalative.

Chemocline oscillations in the Black Sea documented by sedimentary iron isotopes and trace metal patterns

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The reconstruction of chemocline fluctuations in the Black Sea basin using sediment archives is challenging. Thus a reliable and ubiquitous proxy is required, which can be applied to samples independent of their location and water depth in the basin. Recently sedimentary Fe/Al ratios combined with $\delta^{56}\text{Fe}$ values served as a promising proxy for redox interface fluctuations in marine settings. Elevated Fe/Al ratios coupled with low $\delta^{56}\text{Fe}$ values in Black Sea sediments document periods when significant transfer of isotopically light reactive Fe from the shelf to the euxinic basin occurred. The suboxic chemocline, impinging margin sediments allows the lateral transport of Fe^{II}_{aq} across the deep basin. However, to date no published dataset provides high-resolution Fe/Al records of sediment cores from different sampling locations across the Black Sea. Here we show major/trace element data from seven sediment cores sampled at millimeter scale from key locations throughout the entire Black Sea. Synthetic depth profiles were generated by merging the single cores. Furthermore, selected cores were analyzed for $\delta^{13}\text{C}$, $\delta^{56}\text{Fe}$, $\delta^{97}\text{Mo}$, $\delta^{238}\text{U}$, and isorenieratene derivatives.

Our results show two distinctive peaks in the vertical distribution of Fe/Al accompanied by lower $\delta^{56}\text{Fe}$: 1) at the boundary of lithological Units II to III (marine incursion), and 2) in the centre of sapropelic Unit II. The same geochemical signatures reappear throughout Unit I. Our results point towards repetitive chemocline fluctuations owing to changes in the proportion of marine and riverine input into the Black Sea. The rise of the chemocline results from higher input of marine waters, while increased riverine input presumably lowers the redox interface. These results compare quite well with the Eemian sapropel (MIS 5e). Geochemical data from this second sapropel also document a dramatic change from limnic to marine conditions.

Synchrotron rapid scanning X-ray fluorescence of soft-tissue fossils

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Many geochemical and biological analytical techniques have been employed in the identification and quantification of soft-tissues in the fossil record. However, almost all of these techniques require destructive sampling and are unable to provide high resolution, large scale, spatially resolved chemical information from fossil material. Synchrotron rapid scanning x-ray fluorescence (SRS-XRF) developed at the Stanford Synchrotron Radiation Lightsource (SSRL), non-destructively provides highly sensitive, *in situ* and large scale 2D elemental maps at rapid scanning times (~30 secs/cm²) and reveals the distribution of elements present in concentrations below the detection limits of many conventional geochemical techniques. Furthermore, we have uniquely combined x-ray absorption near edge spectroscopy with XRF rapid scanning, to produce maps showing only organic sulfur species. Our recent multi-technique study of fossilised reptile skin (~50 Mya), employing SRS-XRF, Fourier Transform Infrared (FTIR) spectroscopy and Pyrolysis-Gas Chromatography Mass Spectrometry, strongly suggests that remnants of the living organism's original chemistry (protein compounds) are preserved. Additionally, a new taphonomic model has been proposed to explain the survival of these compounds, involving ternary complexation between organic molecules, trace metals and silicate surfaces.

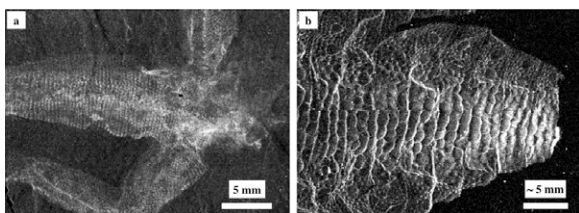


Figure 1: Trace metal loading in a) fossil and b) extant reptile skin.

Fractionation of Cl and Br isotopes during precipitation of salts from their saturated solutions

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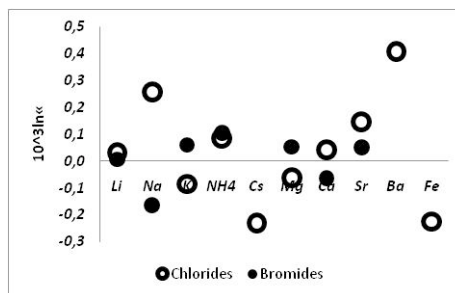
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We determined Cl and Br isotope fractionation of LiCl, NH₄Cl, CsCl, CaCl₂, SrCl₂, BaCl₂, FeCl₃, LiBr, NH₄Br, MgBr₂, CaBr₂ and SrBr₂ between their saturated solutions and first precipitating salts at 23 °C. Considering previous data for NaCl, KCl and MgCl₂ [1] and NaBr and KBr [2] we now have isotope fractionation estimates for common halogen components in marine and terrestrial salt deposits.

¹⁰3lnα for most salts is relatively modest (i.e., a few tenths of a per mil), although clear variations, both positive and negative, are observed.



¹⁰3lnα corresponds to the difference in δ³⁷Cl and δ⁸¹Br between solution and precipitate.

The results obtained in this study can be used to predict Cl and Br isotope fractionation during salt formation in various marine and terrestrial salt deposits. These data can be related to δ³⁷Cl data obtained from evaporites which show that different salts have different ¹⁰3lnα [1] [3].

The observation that ¹⁰3lnα for Cl and Br salts from different elements have different amplitudes and signs might account for the different behaviour of Cl and Br isotopes in natural samples, which show a non-ideal correlation [4] [5].

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From seconds to millennia: Weathering and erosion of the highly dynamic soils of Alpine areas

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Alpine areas are very fragile ecosystems and are strongly sensitive to changing environmental conditions (such as climate warming and land-use change). Soil erosion in the Alps is a well-recognized problem and its temporal scale varies from seconds to millennia. It is identified as a priority for action within the EU (European Union) soil protocol of the Alpine Convention. Steep slopes, extreme climate, fragile soils and the often intensive use of agricultural land characterise the environment of the Alps. There are several approaches to estimating erosion rates in these areas such as modelling using the Universal Soil Loss Equation or empirical determinations using radiogenic isotopes such as Cs or Be or even stable isotopes ($\delta^{13}\text{C}$). Recent results show that heavy-rainfall events as well as erosion processes during wintertime and early spring have a considerable influence on the erosion rates. This explains the often-observed failure of common erosion models for alpine areas - the measured rates are too low. The counter-part to erosion is weathering, keeping the sensitive process of soil formation in balance. Weathering in cold regions has often focused on the notion of 'cold'. As a result of this approach, the process focus has been that mechanical processes predominate and that chemical weathering is temperature-inhibited, often to the point of non-occurrence or extremely slow. Recent investigations show that in cryic, ice-free environments, chemical weathering can be a very active process leading to substantial leaching of chemical components and the formation of secondary weathering products (such as clay minerals). Contrary to popular belief, weathering in cold Alpine regions, including chemical weathering, is not strictly temperature-limited but is rather limited by moisture availability. As a consequence of warming, additional areas will become ice-free in high Alpine areas and subject to weathering, soil formation and erosion. Obvious soil changes must be expected in proglacial areas and at low- to mid altitude sites. Concepts of weathering mechanisms, erosion processes and an overview of recent results from Alpine regions will be presented.

Tracing molecular proxy signals from biological source to sedimentary sink

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The abundances, distributions, and isotopic signatures of biomarker compounds preserved in aquatic sediments are increasingly being used to derive a diverse array of paleoenvironmental and paleoclimatic information. With analytical advances and development of streamlined methodological approaches, there is growing emphasis on biomarker-based reconstructions of past climate at high temporal resolution, and as part of multi-proxy investigations. Crucial to the accurate interpretation of such records is a robust understanding of the provenance of these molecular signals, as well as the timescales associated with signal transfer from biological source to sedimentary sink. While there is often an implicit assumption that the delivery of these signals to the sedimentary archive is virtually instantaneous, there is growing evidence from biomarker-specific ^{14}C measurements that transport may take several hundred to several thousand years. In the case of markers of vascular plant vegetation, storage in soils and at other locations within terrestrial drainage basins may induce significant temporal lags, while in the marine environment episodes of sediment resuspension and redistribution prior to burial have also been inferred to create significant temporal offsets in sedimentary records. The magnitude of such temporal lags may also vary as a function of climate, potentially yielding complex age relationships between proxy records through time. This presentation will describe studies using molecular isotopic ($\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, δD) measurements that seek to explore the interplay between biomarker provenance and signal transmission times in the context of drainage basin properties and past climate variability. The results will be discussed in terms of implications for interpretation of biomarker records and carbon cycling on the continents.

Changes in silicate utilization and upwelling intensity off Peru since the LGM – Insights from silicon and neodymium isotopes

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The Peruvian coastal upwelling area is characterized by one of the most pronounced Oxygen Minimum Zones in the world's ocean. Oxygen concentrations in the water column are controlled by consumption through decomposition of organic matter versus ventilation via ocean circulation. Surface bioproductivity which is dominated by diatoms building their frustules from dissolved silicic acid is a function of both nutrient supply and upwelling intensity. The utilization of silicic acid is reflected by its stable silicon isotope composition ($\delta^{30}\text{Si}$). The lighter isotopes are preferentially incorporated into the diatom frustules leaving the ambient seawater enriched in the heavier isotopes. Thus $\delta^{30}\text{Si}$ values directly mirror silicate availability and the amount of newly supplied silicate with upwelled waters.

Today, the upwelling is strongest near the coast between 10-15°S. There, fractionation is lowest ($\delta^{30}\text{Si} = 2\text{‰}$ for surface water and 1‰ for diatoms, respectively) because the permanent re-supply of nutrients prevents a high degree of fractionation. Outside the main upwelling zone fractionation is higher (up to 2.8‰ in the water and 1.8‰ in the diatoms) indicating slightly increased limitation of silicic acid.

A downcore record from 12°S documents that the main upwelling region has been highly dynamic since the LGM. Biogenic opal concentrations range from 2-31wt%. Accordingly the diatom $\delta^{30}\text{Si}$ data range from 0.4-1.6‰. During the deglacial and early Holocene the $\delta^{30}\text{Si}$ was overall lower than during the late Holocene but much more variable indicating a more dynamic regime. For the late Holocene the low range in $\delta^{30}\text{Si}$ indicate constant upwelling. Low $\delta^{30}\text{Si}$ during the early Holocene would require surface water with $\delta^{30}\text{Si} \sim 1.7\text{‰}$. Today, no surface waters in the area show such low values. Radiogenic Nd isotopes will be applied to address possible changes in source water, either freshwater runoff from the hinterland or enhanced contributions from the south.

For the entire record low $\delta^{30}\text{Si}$ values correspond to low biogenic opal concentrations. The opposite would be the case if silicic acid utilization had been the only driving factor of the $\delta^{30}\text{Si}$ variability. Instead, limitation by other nutrients, e.g. phosphate, during phases of low productivity is more likely.

Strontium and sulfur isotopes in celestite from Likak deposit, SW Iran

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Celestite mineralization in Likak deposit is hosted by Lower to Middle Miocene Gachsaran evaporitic formation. An epigenetic mode of formation via replacement of pre-existing gypsum and anhydrite by later celestite was previously proposed for mineralization [1].

In order to determine the origin of strontium and sulfur for celestite mineralization, 6 samples of the mineral from various outcrops of the orebody were collected for isotopic analyses (2 samples for strontium and 4 for sulfur isotopes). The isotopic analyses were performed by Actlabs (Activation Laboratories Ltd., Canada) using a Triton Multi-collector Mass Spectrometer for strontium, and a VG 602 Isotope Ratio Mass Spectrometer for sulfur isotopes.

Strontium isotopic ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) are 0.708768 and 0.708829 for analyzed samples. These ratios match well with values reported by McArthur and Howarth [2] for Miocene seawater and indicate that Sr was originated from seawater. The celestite samples display $\delta^{34}\text{S}$ values falling in the range of 25.7–27.8. Sulfur isotopic ratios indicate higher $\delta^{34}\text{S}$ values in analyzed samples than those of Miocene seawater [3]. These higher values were probably resulted by bacterial reduction of sulfate [4–6].

Since celestite mineralization has an epigenetic origin, it can be suggested that precursors of the mineralizing fluids were probably produced by evaporation of seawater in a coastal marine setting. As these brines entered into underlying sediments, they leached considerable amounts of Sr from host sediments. Once these Sr-enriched fluids discharged back up into overlying beds containing gypsum and anhydrite, replacement of the beds by celestite were occurred [7].

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Formation of barite chimneys in hydrothermal systems

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Two recently discovered hydrothermal systems at the slow-spreading Arctic Mid-Ocean Ridge system, the Jan Mayen (JMV) and the Loki's Castle vent fields (LCVF) contain barite chimneys of variable composition. Both hydrothermal systems consists of two active vent sites, which is confirmed by elevated hydrogen sulphide concentrations and discharge of high-temperature fluids, reaching 270°C in the JMV and 317°C in the LCVF.

In contrast to the high-temperature vent sites, areas of diffuse venting with emanating clear fluids at slightly elevated temperatures (~20°C) have been found to harbour numerous barite chimneys. The barite chimneys in the JMV are composed of barite, silica and abundant iron, zinc and lead-sulphide minerals, with pyrite representing the dominant sulphides. In contrast, the barite chimneys of the LCVF consist mainly of pure barite with lesser amounts of sulphide minerals.

In addition to oxygen isotopes, this study presents the first multiple sulphur isotope data on barite chimneys in hydrothermal systems. $\delta^{34}\text{S}_{\text{sulphate}}$ and $\delta^{18}\text{O}_{\text{sulphate}}$ values of the JMV barite chimneys are lower than $\delta^{34}\text{S}$ of seawater sulphate and $\delta^{34}\text{S}$ values of extracted sulphides point to a magmatic source. This indicates that these barite chimneys have been precipitated from a mixture of seawater and hydrothermal fluids. $\delta^{34}\text{S}_{\text{sulphate}}$ and $\delta^{18}\text{O}_{\text{sulphate}}$ values for the barite chimneys in the LCVF are higher than $\delta^{34}\text{S}$ values for contemporaneous seawater, and show remarkable differences between the surface and the interior. The highest $\delta^{34}\text{S}_{\text{sulphate}}$ values have been found in the chimney interior, reaching $\delta^{34}\text{S}_{\text{sulphate}}$ values up to +34.9‰. Negative $\Delta^{33}\text{S}_{\text{sulphate}}$ values in combination with positive $\delta^{34}\text{S}_{\text{sulphate}}$ and $\delta^{18}\text{O}_{\text{sulphate}}$ values strongly point to biological sulfate reduction processes, most likely in the sub surface of the LCVF. The presence of filaments within the chimneys (revealed by SEM) and the finding of framboidal pyrite in barite chimneys and underlying sediments in the LCVF indicates that biologic processes caused the observed sulfur and oxygen isotope fractionation.

Sorption of lanthanide ions to mineral surfaces monitored by luminescence spectroscopy techniques

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The distribution of metal ions in the environment is a crucial issue which needs fundamental understanding of the processes involved, e.g., for predicting the safety of repositories for radioactive or chemotoxic waste. In general, the distribution of metal ions is governed by processes like adsorption, desorption, and/or incorporation into inorganic or organic phases, respectively, precipitation from and transport in the aqueous phase. The toxicity of metal ions is not only reflected by its appearance in an environmental compartment, but is determined by its chemical speciation. Therefore, experimental techniques are utile, which allow to monitor the presence and chemical environment of a metal ion at the same time.

The sorption of lanthanide ions on mineral phases, like kaolinite, was investigated by luminescence techniques. As lanthanide ions Europium(III) and Terbium(III) were used because of their outstanding luminescence properties. The influence of salinity and/or the presence of potentially complexing agents on the lanthanide ion's sorption (strength, etc.) was further investigated. As complexing agents low molecular weight organic substances (LMWOS), such as formic and acetic acid, but also potentially chelating agents, like hydroxy propionic acids, were used. Such LMWOS had been identified as constituents of Kerogen isolated from clay minerals and may here distinctly determine the speciation of metal ions. From the luminescence characteristics of the lanthanide ions conclusions concerning their coordination were deduced. Going down to cryogenic temperatures allowed to distinguish between different complex species. Taking advantage of the inter-lanthanide energy transfer made it possible to calculate averaged distances (in the Å to nm range, which extends the observable interionic distance range beyond the first coordination sphere) between sorbed lanthanide ions. Combining the results of the different luminescence techniques deepens the understanding of metal ion sorption on mineral phases, which is a key aspect for understanding transport phenomena of ions (e.g., actinides) in host rock formations.

The suitability of ^{236}U as an ocean tracer

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^{236}U is probably the second most abundant anthropogenic radionuclide (above 10^6 kg produced so far [1]). While previous measurements could identify ^{236}U only in the vicinity of known contaminated sites (Chernobyl, Sellafield, etc.), our measurements are evolving into a consistent picture of the dispersion of anthropogenic ^{236}U . This led to the insight that ^{236}U is a component of the global fallout from nuclear weapons testing and was produced via the $^{238}\text{U}(n, 3n)^{236}\text{U}$ reaction [2].

^{236}U has a well defined source function, is conservative in sea water (residence time approximately 500000 years) and has a sufficiently long half-life (23 Ma) to assure complete mixing in the ocean. The expected natural level below 10^{-13} is negligible compared to the measured anthropogenic ratios. ^{236}U is thus suitable as a tracer for the study of ocean dynamics on a global scale and may in some respects even outperform some more established isotopes.

We analyzed sea water samples from places around the world: the Atlantic ocean ($^{236}\text{U}/\text{U} = (1.9 \pm 0.6) \times 10^{-9}$), the Pacific ocean ($^{236}\text{U}/\text{U} = (5.2 \pm 0.5) \times 10^{-9}$), the Black Sea ($^{236}\text{U}/\text{U} = (3.6 \pm 0.5) \times 10^{-9}$) and the Irish Sea ($^{236}\text{U}/\text{U} = (2.0 \pm 0.02) \times 10^{-6}$). The measured isotopic ratios coincide with established values for contamination by global fallout, except from Irish Sea water, which was clearly influenced by the Sellafield reprocessing plant.

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An absolute reference frame for clumped isotope thermometry

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Analysis of multiply substituted isotopologues of molecules ('clumped isotope geochemistry') presents special challenges to both precision and accuracy. Previous discussions have focused on mass spectrometric precision for these rare species and intralaboratory reference frames. This discipline has spread, demanding interlaboratory standardization. We present a four-laboratory study of the calibration of mass-47 anomalies (Δ_{47} values) in CO_2 (especially extracted from carbonate). We consider: instrument linearity, source fragmentation/recombination reactions (which vary between mass spectrometers and with time and instrument settings), and differences in methods, materials and conditions for sample preparation. We address these problems by developing a method for standardizing Δ_{47} measurements to an absolute reference frame based on theoretical predictions of the abundances of multiply-substituted isotopologues of gaseous CO_2 that has reached a thermodynamic equilibrium at a known temperature. By analyzing CO_2 gases that have been subjected to established laboratory procedures known to promote isotopic equilibration (i.e., heated gases and water-equilibrated CO_2), and by reference to the statistical thermodynamic predictions of equilibrium isotopic distributions, it is possible to construct an empirical transfer function that can then be applied to CO_2 samples with unknown Δ_{47} values. This reference frame may be unique in that it is based on thermodynamic equilibrium, rather than the isotopic composition of an arbitrary reference material. We describe the protocol necessary to construct such a reference frame, the method for converting gases with unknown clumped isotope compositions to this frame, and suggest a protocol for ensuring that reported Δ_{47} values can be compared among different laboratories, independent of laboratory-specific analytical or methodological artefacts. Application of this approach to measurements of CO_2 extracted from several carbonate reference materials results in interlaboratory agreement on their Δ_{47} values to within est. $\pm 0.01\%$, 1σ . Finally, we present a revised paleotemperature scale that applies when using the absolute reference frame described here, as opposed to the previous paleotemperature equation based on data from a single laboratory. More generally, this study presents a model for how interlaboratory standardization might be approached for other 'clumped isotope' measurements.

Strontium isotope fractionation and its application in Earth system sciences

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Taking strontium (Sr) isotope fractionation into account allows the independent and simultaneous determination of paired Sr ratios ($^{87}\text{Sr}/^{86}\text{Sr}^*$, $\delta^{88/86}\text{Sr}$) in silicate and carbonate material. Following this approach the Sr isotope composition of seawater ($\delta^{88/86}\text{Sr}_{\text{seawater}}$: $\sim 0.39\text{‰}$) and marine carbonates ($\delta^{88/86}\text{Sr}_{\text{carbonates}}$: $\sim 0.15 - 0.25\text{‰}$) differ as a function of local environmental parameters and physiological processes which possibly qualifies Sr isotope fractionation as a new proxy in marine geochemistry. This approach extends the well-established application of the radiogenic Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) by an additional dimension and also allows for simultaneous calculation of Sr input and output fluxes of the ocean using complete Sr isotope budget equations. In addition, Sr isotope fractionation is a new isotope tool for the study of organic and inorganic CaCO_3 precipitation mechanisms being sensitive to the precipitation rate at least for calcite.

Recent results indicate that the $\delta^{88/86}\text{Sr}$ value of seawater is controlled by the balance between input and output of shelf-carbonates. In periods of shelf carbonate exposure this input dominates that of Sr originating from silicate weathering. In this regard taking the long residence time (2.5 Ma) and Sr concentration in seawater into account it can be understood why modern and Quaternary corals show about the same $\delta^{88/86}\text{Sr}$ value in the order of $\sim 0.2\text{‰}$. Latter observation qualifies Sr isotope fractionation in marine carbonates as a temperature proxy tool as long as a solid and sensitive temperature- $\delta^{88/86}\text{Sr}$ calibrations can be established.

On Phanerozoic timescales $\delta^{88/86}\text{Sr}_{\text{seawater}}$ follows the general distribution of “calcite seas” and “aragonite seas”, implying a control mechanism by $\text{Mg}/\text{Ca}_{\text{seawater}}$ ratios and further global spreading rates. On shorter timescales in the order of the residence time of Sr in the ocean we observe a strong relationship between the abundance of marine calcifiers and the $\delta^{88/86}\text{Sr}_{\text{seawater}}$ values providing the opportunity to study the disturbances of the ocean carbon budget during mass-extension events as shown for the Ordovician/Silurian and Permian/Triassic boundary, respectively.

Observational constraints on the water and volatile content of planet-forming regions of circumstellar disks

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Models of the protosolar nebula suggest that the Earth formed in an environment too hot for water or volatiles to exist in solid form. Because the Earth is known to possess these elements, investigators posit that they were delivered after the Earth formed by comets, asteroids, hydrated dust grains, or a combination of these mechanisms. Planets in habitable zones around other stars—of which we now have several examples—would require similar mechanisms for water and volatile delivery.

Understanding water delivery to the Earth is a crucial part of the story of our origins. Protoplanetary disks around young stars offer a window through which we can view processes that presumably occurred in our solar system billions of years ago. Study of these disks also illuminates the physical processes by which habitable planets may form elsewhere in the Galaxy.

Recent advances in spectroscopic capabilities both in space and on the ground enable probes of warm water vapor and volatile material across a range of excitation conditions. I will review observations of protoplanetary disks that reveal the spatial distribution, temperature, and column density of gas-phase water and volatile material in 'terrestrial' regions. The presence of these molecules in warm, inner disk regions implies transport from cooler regions at larger stellocentric radii, and presents observational constraints on models for water and volatile delivery to terrestrial planets.

Geoenvironmental factors evaluate the underground waters in the eastern desert of Egypt

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New areas of utilization had to be developed within the desert area where the underground water reservoir could be used. Therefore, selection of good localities for drilling new water wells suitable for human use and how to use the present water wells is very important in any planning and development. The aim of this paper is to ultimate the benefits of the water wells and delineate their risk. And intends to contribute in developing a suitable methodology for the founding good new water wells. In this study, we proposed the following geoenvironmental factors to ultimate the water wells availability and quality; i) Impact of the surrounded (host) rocks and the type of aquifer sediments. ii) Impact of mining and quarirs activities and mineralized body in the drained basin. iii) Impact of well's situation in site of water flow in it's drained basin. Eastern Desert of Egypt occupies more than 230, 000 km². Hundred important water wells had selected in Eastern Desert to investigate the impact of suggested geoenvironmental factors. There are 96 gold mines in Eastern Desert, in spite of gold mining activities started in the Pre-Dynastic period of the Egyptian history (4000yearsBC) and continued up to the recent years. Besides ochre (iron oxides) and several Pb-Zn mines.

New geomorphological and drainage basin maps for Eastern Desert had been prepared using Landsat ETM images and revise the published geological and topographic maps. Correlation between the published chemical analyses of the underground water for 82 wells on one side and the host rock forming minerals, mining activities, position in the drained basin and the type of the aquifer on the other side.

Elements, when leached from mining wastes are concentrated in certain parts of a drainage basin by flash flood. And contaminate the underground water with elements both from the ore body and mining activities such as Pb, Zn, Cu, and Fe and dissolved materials are high content in these wells. The alkaline water found at the footslopes of syenite mountaines. Abundance from clay minerals in underground water found at granite and syenite terrain as a result of weathering of feldspars. This study monitored that the underground water analyses reflected the rock forming minerals and mining activities in it's surroundings. The aquifer type has considerable significance. There are good water from several wells regarding to these factors. This article elucidates that the proposed impact of the mentioned geoenvironmental factors is actually, the first attempt in the study of the subject in Egypt. Therefore, it is strongly advisable to perform an geoenvironmental impact assessment before starting any drilling for new water wells and before use the present wells and have to put in data base.

Gold and platinum group mineral at Bleida Far West, Anti-Atlas, Morocco

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The Bou Azzer-El Graara inlier in the Anti-Atlas is well known for its Co-As deposits with gold as a by-product, and the abandoned Bleida Cu deposit. Recent prospecting by Reminex led to the discovery of a significant gold-palladium mineralization some 7 km NW of the former Bleida copper mine (-6.5173038, 30.3923419).

At Bleida Far West, Au-Pd mineralization is hosted by hydrothermally altered amphibolites and chlorite schists. The mineralization occurs in a 7 by 5 km wide corridor, and is associated with intense silicification and numerous, narrow, quartz-dominated, carbonate-bearing veins. Close to surface, the mineralization is hosted in weathered, soft, clayey and powdery material rich in Mn- and Fe-oxides/hydroxides with visible gold.

The pristine mineralization is virtually sulfide-free. Gold (grains up to 400 μm in diameter) is associated with hematite, quartz, calcite, barite, epidote and chlorite. Individual gold grains and grains within individual samples are usually chemically homogeneous. The composition of gold analysed by EPMA (n = 82) ranges from 79 to 93 wt.% Au, 6 to 19 wt.% Ag, and 0.5 to 7 wt.% Pd. The gold grains are intergrown with a distinct suite of PGM, namely mertieite-I [Pd_{5+x}(Sb,As)_{2-x}], keithconnite [Pd₂₀Te₇], palladseite [Pd₁₇Se₁₅], and sperrylite [PtAs₂].

A genetic model on the genesis of the Bleida FW mineralization must bear in mind that the gold is associated with hematite and barite, not with sulfides. The combined geochemical and mineralogical evidence so far suggests a relatively low-temperature hydrothermal origin of the gold from oxidizing fluids, related to syn-tectonic quartz-diorite intrusions, or other, still imprecisely known events.

Secondary crustal effects on MORB composition at the Kolbeinsey Ridge

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We present results for the systematic crustal alteration of basalts from the shallow, slow-spreading Kolbeinsey Ridge (67°05'–70°26'N). Age-constrained Kolbeinsey lavas are isotopically depleted (e.g. $^{87}\text{Sr}/^{86}\text{Sr} = 0.70272\text{--}0.70301$) with ($^{230}\text{Th}/^{238}\text{U}$) = 0.95–1.30, low U (≥ 11 ppb), and low Th (≥ 33 ppb). The basalts have a narrow range of ($^{230}\text{Th}/^{232}\text{Th}$) ratios (1.20–1.32) over a large range in ($^{238}\text{U}/^{232}\text{Th}$) (0.94–1.32), producing a horizontal array on a ($^{230}\text{Th}/^{232}\text{Th}$) vs. ($^{238}\text{U}/^{232}\text{Th}$) diagram. However, we observe that the range of ($^{230}\text{Th}/^{238}\text{U}$) (0.96–1.30) is inversely and nearly linearly correlated with ($^{234}\text{U}/^{238}\text{U}$), reflecting shallow crustal alteration of the basalts. Variations in U and Th concentrations and Cl/K₂O ratios are not systematic, indicating a combination of crustal alteration mechanisms. For example, samples with elevated Cl/K₂O ratios but no elevated ($^{234}\text{U}/^{238}\text{U}$) ratios have likely experienced the addition of subsurface brines with low oxidation states and, thus, low U solubilities; the addition of those fluids is not expected to systematically affect the U isotope composition of the basalts. $^{87}\text{Sr}/^{86}\text{Sr}$ and ($^{234}\text{U}/^{238}\text{U}$) isotope variations, on the other hand, support the systematic addition of material from hydrothermally altered crustal rocks to the basalts.

Unaltered Kolbeinsey lavas have high ($^{230}\text{Th}/^{238}\text{U}$) values (≥ 1.2), which are consistent with melting in the presence of garnet and with production of thick ocean crust by large degrees of melting.

Fractionation of Li and Mg isotopes in mantle derived materials— Promise, perils and progress

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Li and Mg provide an interesting pair of elements with which to explore the process that influence high temperature fractionation of cationic species in geological environments. There are large relative mass-differences between the isotopes of Li (17%) and Mg (8%) that should promote discernible fractionations. Both elements are hosted in major lattice sites in common mantle minerals and so the energetics of exchange between different minerals can be reasonably well understood. Neither show multiple valences over mantle conditions, that can dominate fractionation behaviour. The value of understanding the processes that lead to their high temperature fractionations, aside from intrinsic curiosity, is that signatures related to processes of planetary differentiation and recycling may be discerned over later magmatic influences

The importance of diffusion in isotopic fractionation in the Li system has been highlighted in a number of earlier studies. Our new *in situ* studies re-emphasise the complexity and magnitude of fractionations that can occur by late-stage diffusion. Moreover, we show that Mg isotopic variations in bulk xenoliths co-vary with those of Li. Again diffusion is implicated although it is not obvious what drives the ingress of Mg. We suggest it may be related to volatile loss *en route* to surface. In samples uninfluenced by diffusive fractionation, as identified from unzoned, mineral Li isotope profiles, natural fractionation factors can be gleaned from analyses of co-existing bulk minerals. Clinopyroxenes are heavier in both Li and Mg systems, as predicted in the latter by computational studies of equilibrium partitioning. More experimental data could yield better constraints over a wider range of conditions.

Widespread synchronous volcanism on the Snake River Plain

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Rhyolitic volcanism in the central Snake River Plain (SRP) represents the early history of the Yellowstone hotspot. An ignimbrite flare-up has been recognised in the SRP between 11.7 and 10.2 Ma [1] during which >75% of the total volume of ~20,000 km³ of high temperature rhyolitic magma was erupted. Ignimbrites of the central SRP are almost identical in field appearance being intensely welded with an anhydrous mineral assemblage, so geochemical methods are required to distinguish between magma batches. Here, we combine field constraints, mineral and glass compositions, stable isotopes, and new high precision ⁴⁰Ar/³⁹Ar geochronology to fingerprint magma batches and investigate the timing and distribution of volcanism during the flare-up. Our results indicate that five similar but subtly different magmas were erupted and deposited to both the north and south of the plain beginning with Brown's Bench 4 (11.59 ± 0.081 Ma, n=31, 2σ) and ending with the Tuff of Fir Grove (11.14 ± 0.13 Ma, n=19, 2σ). Magma batches may be distinguished by the presence of multiple compositional populations of both pigeonite (Mg# 9-17) and augite (Mg# 8-22) and variation in ilmenite compositions. All five ignimbrites exhibit the characteristic depletion in δ¹⁸O observed in the central SRP with feldspar values between 1.96 and 2.97‰.

The widely dispersed (>100 km E-W) and geographically limited nature of some of the ignimbrites suggests they were erupted from different sources currently buried beneath younger basalts within the SRP. These results suggest that the currently accepted model of discrete 'eruptive centres' requires reconsideration. The high precision geochronology shows that during the flare-up ignimbrite-forming eruptions were occurring in the central SRP at a frequency more than 7 times that of the present Yellowstone volcanic field and 5 times that of the Heise eruptive centre. We propose that the opening of the western Snake River Plain graben, itself exploiting a pre-existing crustal weakness illustrated by the Vale fault zone directly to the NW, caused lithospheric thinning and resulted in the increased eruptive frequency.

[1] Bonnicksen *et al.* (2008) *Bull. Volc.* **70**,315-342.

Geochemical alteration of fracture geometry during leakage of CO₂

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A series of three flow-through experiments were performed on artificially fractured caprock samples to investigate fracture evolution during simulated leakage of CO₂-acidified brine. The core samples are from the Amherstburg limestone, which is the caprock for a CO₂ storage demonstration project in northern Michigan, USA.

The evolution of fracture aperture was monitored in real time using X-ray computed tomography (CT). Before and after the experiment, 3-D reconstructions of the fracture structure, aperture and surface roughness were examined at higher resolution via micro X-ray CT. The cores were then sectioned and examined with scanning electron microscopy, X-ray fluorescence and micro X-ray diffraction.

Although all three samples were of nearly identical mineralogical composition, the brine flow rates, initial brine compositions, and initial fracture permeabilities differed across the three samples. These differences in flow conditions and fluid composition generated different degrees of fracture deterioration. The first run resulted in substantial erosion of the fracture surface, while the second run had a decrease in fracture permeability that may be attributed to mineral precipitation along the fracture.

Spectroscopic analysis of the samples after CO₂-brine flow demonstrated preferential calcite dissolution. Mineral spatial heterogeneity coupled with the preferential dissolution of calcite led to non-uniform degradation along the fracture and an increase in surface roughness. In areas where calcite is intermixed with dolomite and other silicate minerals the dissolution of calcite leads to the formation of a degraded zone along the fracture boundary, resulting in a smaller increase in fracture aperture.

The potential mineral precipitation found in the second run is in stark contrast to the rapid mineral dissolution found in the first and suggests a complex interplay of mineral spatial heterogeneity, brine composition, and flow conditions controlling caprock fracture evolution. Results from this study will be used to frame a discussion on how flow through caprock fractures may be influenced by geochemical alteration of fracture geometry.

Deglacial southern ocean ventilation history from a benthic foraminiferal $\delta^{13}\text{C}$ Transect

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Abrupt climate changes during the last deglaciation are associated with corresponding changes in Southern Ocean overturning circulation and ventilation, particularly during the Antarctic Cold Reversal (ACR). Herein, we present high-resolution, mono-specific (*P. wuellerstorfi*), benthic foraminiferal $\delta^{13}\text{C}$ records from a depth transect of cores to reconstruct ventilation changes in the New Zealand region of the Southern Ocean. The cores span depths of; 600m (RR0503 87TC/87JPC), 1200m (RR0503 79JPC), 1600m (RR0503 83TC/83JPC), 2045m (H214;), 2500m (RR0503 125JPC), and 3800m (RR0503 41JPC). Age control is based on tephrastigraphy, and additionally constrained by $\delta^{18}\text{O}$.

During the last glacial period, the difference in $\delta^{13}\text{C}$ values ($\Delta\delta^{13}\text{C}$) between 600 and 3800m, is $\sim 1.7\text{‰}$, significantly higher than during the Holocene ($\sim 0.7\text{‰}$), implying reduced glacial ventilation. In the early deglaciation, $\delta^{13}\text{C}$ increased at deep sites, suggesting increasing ventilation. Glacial $\delta^{13}\text{C}$ values at 1200m lie evenly between the values of the deeper sites (1600 – 3800m) and the shallowest core (600m), suggesting a distinct glacial intermediate water mass. During the ACR, $\delta^{13}\text{C}$ at 1200m increased and converged with values at 600m, suggesting that a single water mass bathed 600 – 1200m. Following the ACR, $\delta^{13}\text{C}$ values at 1200m again become distinct from the shallow and deep sites and the $\delta^{13}\text{C}$ in the deeper cores increases rapidly (by $\sim 0.5\text{‰}$), reducing the $\Delta\delta^{13}\text{C}$ to $\sim 1.0\text{‰}$ post-ACR.

These results indicate a step-wise change in stratification and ventilation across the ACR boundary, suggesting the ACR had both a short term and enduring impact on shallow interior ventilation in the Southern Pacific.

Characterisation of the transfer and biodegradation of chloroacetamide herbicides in lab-scale wetlands

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Chloroacetamide herbicides are extensively used in the USA and in Europe for the control of annual grasses and broad-leaved weeds in a variety of crops including maize, sugar beet and sunflower. The major dissipation route for metolachlor, alachlor and acetochlor herbicides appears to be microbially-mediated degradation in soil ecosystems. However, detailed knowledge about their transfer, mitigation and biodegradation in wetland systems is scarce. Here, we examine the transfer and attenuation of metolachlor, acetochlor and alachlor in wetland systems, mainly focusing on their *in situ* biodegradation under different conditions and the characterisation of the microorganisms involved. In order to reach an integrated understanding of chloroacetamides attenuation processes, our investigations will include two different scales. The mesocosm scale experiment will examine the transport and biogeochemical changes under field-like conditions, whereas the microcosm experiment will involve aerobic and anaerobic enrichment cultures set-up in a sediment extract medium and a minimal medium. The biogeochemical dynamics of the lab-scale wetland systems will be characterised using hydrochemical, biomolecular and compound-specific isotope analyses (CSIA). Changes in herbicide concentrations, their enantiomeric ratios and some of their degradation products will be assessed over the flow path and over time. In parallel, changes in the structure of the microbial communities present in lab-scale wetlands will be characterised using PCR-T-RFLP analysis. CSIA methods will be developed to characterise the biodegradation of chloroacetamide herbicides during their transfer in wetland systems.

Formation of layered Fe(II)-Al(III) hydroxides during reaction of Fe(II) with γ -Al₂O₃ and montmorillonite

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The biogeochemical cycling of iron in aqueous geochemical environments is intimately linked to the cycling of carbon, nitrogen, phosphorus and sulfur, and strongly impacts the solubility and speciation of trace metal and metalloids in these systems. In riparian zones, reductive dissolution of Fe(III)-(oxyhydr)oxides mediated by soil microbes leads to a buildup of high concentrations of dissolved Fe(II) in soil solution and concurrent release of sorbed contaminants. The fate of released Fe(II) is at least partially controlled by sorptive interactions with Al-oxides and phyllosilicates minerals in the soil matrix. Here, X-ray absorption spectroscopic evidence is presented for the formation of Fe(II)-Al(III)-layered double hydroxide phases during reaction of Fe(II) with Al-oxide and montmorillonite clay. These phases form fast (on time scales < 24 h) and are therefore expected to be a major sink for Fe(II) released during reductive dissolution of Fe(III)-oxides. In addition, owing to small particle size, layered structure, and high Fe(II) content, these phases are likely to be highly reactive towards redox-active contaminants such as Cr(VI), and may control retention of divalent metals such as Ni(II) and Zn(II) through adsorption and coprecipitation reactions. The research presented here characterizes formation of these phases in relation to observed macroscopic uptake trends of Fe(II) as a function of Fe(II) concentration, pH and reaction time.

Cycling of nitrogen in the Namibian coastal upwelling system – The stable isotope view

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Nitrogen is a key element in regulating biological processes in the ocean, and the history of the nitrogen cycle under past conditions on Earth is of high relevance for paleoceanographic and paleoclimate studies. The ratio of the two stable N-isotopes (¹⁵N/¹⁴N; expressed as $\delta^{15}\text{N}$ versus air N₂) preserved in sediments is commonly assumed to reflect the isotopic composition of N-sources, or the extent of assimilation by phytoplankton. But although $\delta^{15}\text{N}$ is widely appreciated as one of few available proxies to reconstruct marine nutrient cycles in the geological past, there are several biases on the $\delta^{15}\text{N}$ of sedimentary records. Here we explore the dynamics of nitrogen isotopic composition in several compartments of reactive nitrogen in a depositional setting characterized by extreme gradients in $\delta^{15}\text{N}$ of nitrate, suspended matter and surface sediments – the coastal upwelling area offshore Namibia. The gradient observed in $\delta^{15}\text{N}$ of surface sediments mirrors the state of oxygen depletion in the water in contact with sediments, as well as changes in source nitrate, in water-column denitrification, in particle advection along the shelf break, and in dominant upwelling mode (coastal versus shelf break upwelling). Based on data of nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in several seasonal sampling campaigns, we attempt to isolate possible diagenetic effects by determining $\delta^{15}\text{N}$ of suspensions and surface sediments in conjunction with indicators of organic matter quality (i.e., the degradation index of amino acids, C-normalized amino acid concentrations) in the pronounced oxygen gradient of the region. Besides sharpening the $\delta^{15}\text{N}$ as a proxy for the geological past, the data also allow us to examine some basic biogeochemical concepts underlying nutrient stoichiometry in the ocean. This is important in light of the expected increasing importance of upwelling processes for the supply of nutrients to the surface ocean.

Noble gas isotope fractionation during air-sea exchange: A tracer for mechanisms that determine N_2/Ar ratios in the ocean

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Our observations indicate that the N_2/Ar ratio in the world's ocean increases from near equilibrium with the atmosphere at the surface to ~ 1.5 % supersaturation at depth (~ 1000 m) and the values in deep waters increase from the Atlantic to Pacific Ocean by ~ 0.5 %. The reason for the increase is a combination of air-sea exchange during formation of subsurface waters and denitrification below the euphotic zone. In order to separate these two processes one must understand bubble processes that occur during gas exchange. The change in gas ratios is more strongly influenced by small bubbles that totally collapse than larger bubbles that exchange gases across the bubble-water interface.

The isotope ratios of argon ($^{40}Ar/^{36}Ar$) and neon ($^{22}Ne/^{20}Ne$) are sensitive to the mechanisms of bubble processes because kinetic isotope fractionation caused by molecular diffusion coefficient differences is a tracer for the bubble exchange mechanism. We have determined the kinetic isotope fractionation factor during gas exchange for argon and neon in laboratory experiments to be $-3.3 \pm 0.3 \text{ ‰}$ and $-6.7 \pm 0.3 \text{ ‰}$ respectively. These values agree to within the estimated error of theoretical calculations [1] if one assumes the gas exchange process is proportional to the square root of the molecular diffusion coefficients. Using the measured fractionation factors in a gas exchange model [2] to determine the sensitivity of argon and neon isotope ratios to bubble processes suggests that neon isotopes might be a useful tracer for determining the importance of the bubble exchange mechanism. The changes, however, are small—on the order of 0.1-0.2 ‰ -- and to our knowledge, highly accurate neon isotope ratios in seawater are yet to be determined.

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Rock alteration and element transfer during formation of U deposits related to Na-metasomatites in the Ukrainian Shield

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The Central Ukraine U Province is situated in the Ingul Megablock and along its eastern border in Kryvyi Rig – Kremenchug syncline zone of the Ukrainian Shield. The Province includes about 20 U deposits and numerous U showings hosted by Palaeoproterozoic metamorphic and magmatic complexes. Two of these deposits (the Zhovta Richka and Pervomayske deposits) already have been exhausted but four U-deposits in the altered granitic rocks (Vatutynske, Novokostantynivka, Michurynske and Central deposits) are currently operated. Rock samples were selected in underground mines and from drillcores, were examined for mineral parageneses using optical microscopy and after agate mortar crushing were analysed for major and trace elements with ICP-AES/MS techniques (CNRS, Nancy, France). Element transfer was estimated using simply binary and/or isocon diagrams [1]. Multistaging of metasomatic alteration of the host rocks (dominantly granites and migmatites) provided sequential changing of mineral parageneses from earlier to later mineral parageneses. The earliest alteration represents successive transformation of the host granitoids into chloritized granites and episyenites, which were progressively dequartzified and eventually transformed into aegirine and aegirine-reibeckite albitites due to progressive K-Na exchange between hydrothermal solution and the rocks. Na, V, Ca and Sr were the most prominent extrinsic elements introducing in the host rocks during this stage of the alteration whereas Si, K and Rb were ejected. Next stage of hydrothermal activity provided carbonate metasomatism with partial leaching of the albitites and crystallization of garnet, epidote, calcite, magnetite and either Mg-amphiboles or phlogopite mineralization with reverse depletion in Na. Na, Si, V, Ba and P were transferred out of the albitite bodies but U, K, Rb, Ca, Sr, Mg, U, Mn, Zr, Hf and Co were added.

[1] Grant (1986) *Econ. Geol.* **81**, 1976-1982.

Impact of interfacial free energy on weathering rates

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The natural weathering rates of primary minerals can be orders of magnitude lower than the rates of mineral dissolution found in laboratory experiments. As primary dissolution rates are thought to be determined by the rate of secondary mineral precipitation, understanding the factors controlling precipitation rates could be the key to resolving this apparent discrepancy. Using model calculations we demonstrate that the effects of interfacial energy in systems close to equilibrium, and which possess a large number of micron and nanometer scale crystals, can have a critical impact on net mineral precipitation rates [1]. Net rates can be much lower than those predicted by standard kinetic formulations; moreover, when the proportion of small crystals is high enough, net dissolution can dominate even when the system is supersaturated with respect to large crystals. Importantly, secondary minerals that form from the incongruent dissolution of primary phases are often submicron in size, and field conditions are often far closer to equilibrium than those typically encountered in laboratory experiments. Thus, we propose that standard rate models - which do not account for interfacial energy effects in small crystals - may be unsuitable to describe reaction rates in weathering systems.

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Metalliferous organic-rich black shales: Where do the metals come from?

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The amount of metal contained in a metalliferous black shale (MBS) can rival or surpass any ore deposit. Currently anomalous metal and carbon contents of these shales are thought to be controlled solely by ordinary oceanographic processes. Elevated metal and carbon contents of these shales are considered to reflect anoxic, high productivity conditions that optimize extraction of metals from normal seawater.

This explanation is challenged by the lack of modern analogs of ancient MBS. Despite intense study, modern euxinic environments of high productivity fail to form sediments with comparable metal enrichments. Moreover, mass balance constraints that consider the total mass and recharge of metal to the ocean, ocean circulation, and sedimentation rate suggest that typical seawater may not be an adequate source for the mass of metal in some MBS.

An alternative metal supply is apparent in the fluids that form, syndepositional exhalative (sedex) deposits. The metal supplied by the discharge of these hydrothermal fluids into ocean basins can be shown to surpass global riverine fluxes. The metal mass in a sedex deposit requires discharge of 1000's of km³ of warm saline fluid over a period of 10's ky. The large volume would have impacted ocean chemistry far beyond the extent of the deposit.

A genetic link between MBS and sedex deposits is reinforced by their common occurrence in age correlative strata. Although this temporal relationship has been previously ascribed to euxinic conditions necessary to form sedex deposits, the sedex fluids may, themselves, have enhanced or caused euxinic conditions.

An overlooked aspect of sedex systems is the flux of nutrients (i.e. NH₄, reduced C, trace metals, Ba, Si) added to the oceans by the ore fluids that may exceed the entire modern riverine flux. Such fertilization would undoubtedly promote massive increase in bioproductivity and spur basin-wide anoxic/euxinic conditions. Overall, the enormous flux of nutrients and metals delivered to the ocean by sedex systems may provide a plausible explanation for the enigmatic metal-rich end members of MBS.

Cationic polymerization of isoprene on cloudwater droplets

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We show that gas-phase isoprene is readily protonated and subsequently polymerized by collision with liquid microjets surface of mildly acidic water ($1 < \text{pH} < 4$) within ~ 10 ms. Kinetic isotope effects for the products formation were determined to reach up to 7, showing the direct evidence that the observed phenomena are due to a truly interfacial reactions initiated by proton on water. Since such reactions only occur at superacidic condition in homogeneous bulk media (e.g., $\text{pH} < -1$) or in pure gas phase, the surface of ambient atmospheric aerosol particles will behave as an unusual catalyst for reactive uptake of global gaseous unsaturated hydrocarbons.

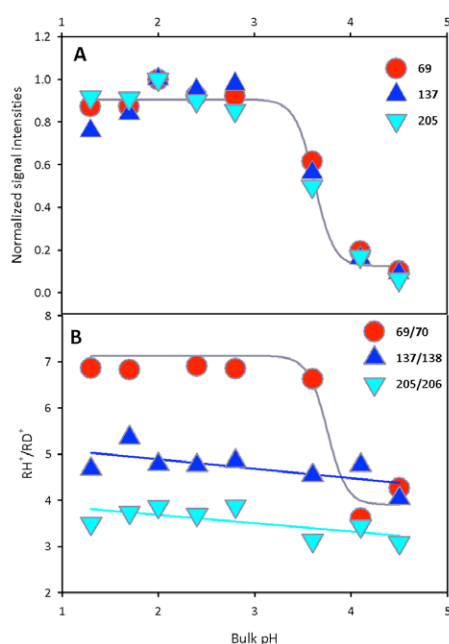


Figure 1: A: Signals IsoH^+ ($m/z = 69$), $(\text{Iso})_2\text{H}^+$ (137), and $(\text{Iso})_3\text{H}^+$ (205) from protonation/polymerization of isoprene produced on $\text{H}_2\text{O}:\text{D}_2\text{O}$ (50/50 = vol/vol) microjets exposed to 88 ppmv isoprene(g) for ~ 10 μs as a function of bulk pH. B: Kinetic isotope effects (KIE) for the products of isoprene (g) on $\text{H}_2\text{O}:\text{D}_2\text{O}$ (50/50 = vol/vol) microjets exposed to 88 ppmv isoprene (g) as a function of bulk pH. All experiments in 1 atm $\text{N}_2(\text{g})$ at 293 K.

Testing the use of detrital rutile to investigate HP/UHP rocks

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Accessory rutile generally is the main host of Ti in HP/UHP metamorphic rocks. It is also a major carrier of HFSE, providing a potential tracer of contrasting tectonic processes. For example, the Zr-in-rutile geothermometer has now been widely and successfully applied to HP rocks, and Cr/Nb ratios have been used to distinguish between different bulk composition of the host rock. Moreover, rutile is a robust mineral in sedimentary environments and is common as an accessory phase in sandstones. Therefore, its potential as a detrital tracer of HP metamorphism is high. Metamafic and metapelitic rocks from two case studies located in Syros, Greece and the Western Alps, both settings displaying HP/UHP conditions, have been sampled together with sediments that resulted from the erosion of these rocks in beach and river catchments. The geochemical correlation of rutile between source rocks and sediments is assessed based on its HFSE budget.

This study aims to establish geochemical signatures of rutile that are characteristic for detrital grains sourced from HP/UHP rocks formed in subduction zones. The Zr-in-rutile thermometer [1, 2] provides peak metamorphic temperatures for the investigated samples that are coherent with published peak temperatures for the respective metamorphic sequences. In addition, the calculated temperatures are independent of the source rock lithologies, i.e., the presence or absence of quartz. The T histograms for the Western Alps indicate a low-T peak, suggesting the blueschists, eclogites and Dora Maira rocks are dominant, and not the high-T Ivrea rocks, as expected. Cr/Nb ratios have been employed successfully and *in situ* analysis fall strictly into the mafic (for Syros) and pelitic (for the Western Alps) source rock fields [3, 4, 5].

[1] Zack *et al* (2004b) *CMP* **148**, 471–488. [2] Watson *et al* (2006) *CMP* **151**, 413–433. [3] Zack *et al* (2002) *Chem. Geo.*, **184**, 97–122. [4] Zack *et al.* (2004a), *Sed. Geo.*, **171**, 37–58. [5] Meinhold (2010) *E-S Rev.* **102**, 1–28.

Characterizing sources of airborne mineral dust, in Iraq

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The purpose of the Enhanced Particulate Matter Surveillance Program (EPMSP) was to provide scientifically founded information on the chemical and physical properties of airborne mineral dust and other particulates sampled in the Middle East. Aerosol [1, 2] and bulk soil [3] samples were collected during a period of approximately one year at 15 Middle East sites – including Djibouti, Afghanistan, Qatar, United Arab Emirates, Iraq, and Kuwait. Collocated low volume particulate samplers, one each for the total suspended (TSP), less than 10 µm in aerodynamic diameter (PM₁₀) and less than 2.5 µm in aerodynamic diameter (PM_{2.5}) particulates were deployed at each of the sites and operated on a “1 in 6 day” sampling schedule. The filters were chemically analyzed for their elemental and ion contents, as well as for their elemental (EC) and organic carbon (OC) fractions.

This presentation reports on the data mining of chemical results - by applying Principal Components Analysis (PCA) and Positive Matrix Factorization (PMF) to chemical data from Teflon membrane and quartz fiber filter sets collected at six sites in Iraq (Balad, Baghdad, Tallil, Tikrit, Taji and Al Asad).

From the PMF modelled results it is evident that there are substantial differences in mineral dust compositions amongst the six Iraq sites and between the PM₁₀ and the PM_{2.5} size fractions. This is related to dissimilarities in the local geology and soil types, as well as different particle size distributions. Although regional mineral dust sources are similar for all six sites, the aerosols at the height of the sampler inlets are substantially modified by local dust representative of the local soils at or close to the sampling sites, exacerbated by dust from agricultural activities, roads, and other local dust sources.

[1] Engelbrecht *et al.* (2009a) *Inhalation Toxicology* **21**, 297-326. [2] Engelbrecht & Derbyshire (2010) *Elements* **6**, 241-246. [3] Engelbrecht *et al.* (2009b) *Inhalation Toxicology* **21**, 327-336.

Allanite petrochronology in high-pressure rocks

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Allanite is a REE- and Th-rich epidote widespread in greenschist to eclogite facies rocks. Its prograde mineral reactions commonly produce distinct growth zones, which can be directly related to PT-conditions. In favorable cases, Th-U-Pb isotope analysis (by LA-ICP-MS or ion microprobe) allows such growth zones to be dated.

Improved LA-ICP-MS analysis (line raster laser ablation, ²⁰⁴Pb-based common lead correction) yields accurate Th-Pb and U-Pb ages with no need for matrix-matched standardisation. The analytical errors imply realistic 2σ-age uncertainties of ~1%.

A multicomponent solution model formulated for allanite was tentatively calibrated, based on the limited experimental data available as well as select natural phase relations. Phase diagrams calculated for a range of typical compositions comply with mineral reaction sequences and established PT-wisdom from various metamorphic systems. The stability limits obtained confirm that allanite is very useful for blueschist and eclogite facies rocks. Computed REE-partitioning with other REE-phases agrees reasonable well with distribution coefficients observed in high-pressure samples.

Several case studies in LT-eclogite facies metagranitic and -sedimentary samples from the Sesia Zone (Western Alps, Italy) are presented. These demonstrate the potential power of allanite petrochronometry [e.g. 1], but also indicate limits and possible pitfalls: Detailed petrography is needed to define which stages and PT-conditions are dated, and microstructural observations should be integrated where possible. It is critical to obtain REE-patterns for each allanite growth zone and to characterize all mineral inclusions. Common lead contents can be so high as to make dating unrealistic.

Allanite recrystallisation behaviour is not well understood, and relics (e.g. igneous cores) commonly occur. Microchemical characteristics (Th/U, Sr) help to distinguish their origin. In relatively dry lithologies, the robust mechanical properties of allanite can preclude recrystallisation, even in high strain shear zones. By contrast, allanite has excellent potential as a chronometer for mylonites, where hydrous fluid commonly leads to recrystallisation even at T as low as 400°C.

[1] Rubatto *et al.* (2011) *Nature Geosci.*, 10.1038/NGEO1124

Modeled response in radiative properties of shallow convective clouds due to perturbations in meteorological state variables and atmospheric aerosol loading

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In order to quantify aerosol indirect effects in observational data it is necessary to minimize the impact from other cloud-controlling variables. The vast amount of meteorological data from operational atmospheric analysis data (or re-analysis data) combined with retrieved aerosol characteristics from satellite, provides an opportunity to compare cloud properties under similar meteorological conditions but with a different aerosol signature. However, even when keeping meteorological variations at a minimum with respect to a mean atmospheric state, the sensitivity of clouds to small perturbations around this mean state is not well known [1]. Hence small variations in meteorology may correlate both spatially and temporally with small variations in the aerosol concentration which could explain a certain fraction of the observed relationship between aerosols and clouds.

The aim of the present study is to 1) identify the sensitivity of cloud fraction and cloud albedo to small perturbations in meteorological conditions and compare this to the sensitivity induced by increasing aerosol number concentrations and 2) estimate the range of variability in observational data of meteorological variables permitted to determine a clear and unambiguous signal in cloud fraction and cloud albedo due to aerosols. A cloud-resolving model is used to simulate a large ensemble of isolated shallow convective clouds where the vertical profiles of zonal wind, temperature and water vapor mixing ratio as well as initial profiles of accumulation and Aitken mode aerosols are perturbed.

[1] Stevens and Feingold (2009) *Nature* **461**, 607–613.

Hydrothermal Co-Ni mineralization, associated with serpentinized peridotites: Bou Azzer, Morocco

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The Co, As (Ni, Ag, Au) ores of the Bou Azzer district comprise an unusual type of vein-style deposit, associated with mantle peridotites of a Neoproterozoic ophiolite. Two types of Co-rich mineralization are exploited: (1) Veins located at the contact between serpentinites and wall rocks; (2) Veins in dioritic wall rocks, extending up to 400m from the serpentinites. From early to late, the mineral succession in both types is : (1) Ni-arsenides (rammelsbergite, pararammelsbergite); (2) Co-arsenides (safflorite, skutterudite), in some cases with native gold; (3) Fe-Arsenides (löllingite); (4) sulfoarsenides (gersdorffite, cobaltite, arsenopyrite); (5) sulfides and sulfosalts (chalcopyrite, sphalerite, tetrahedrite, tennantite), in some cases with native bismuth and silver; (6) chlorite with molybdenite with minor brannerite and late native gold. The gang minerals are essentially quartz, calcite and dolomite. Fluid inclusion studies indicate complex brines belonging to the system (Na, Ca, K, Ba, Cl). Equivalent weight salinity ranges from 34.5 wt. % and 40.5 wt. %. Homogenization temperatures range from 225 °C to 195°C. Co and Ni are proposed to have been leached from the serpentinites. However, the origin of the arsenic is poorly constrained. Derivation from the mantle rocks would imply very high fluid-rock ratios. Alternatively, As could be derived from crustal rocks underlying the ophiolite.

Comparison of mercury bioaccumulation within a trophic-web for pristine and anthropogenically contaminated aquatic ecosystems

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Lake Baikal-Angara River aquatic ecosystem includes natural basin of Lake Baikal (LB) with more than 360 inflow rivers, and few artificial basins such as Irkutsk, Bratsk and Ust'-Ilimsk Water-Reservoirs located downstream the only outflow Angara River. The main anthropogenic sources of Hg in the region were two chemical industrial factories "Usol'ekhimprom" and "Sayanskkhimplast", located on the shore of the Bratsk Water-Reservoir (BWR). Anthropogenic utilization of mercury is a global health issue due to its high degree of mobility, toxicity and bioaccumulation of methylmercury through the food-web.

Sediments, water, zoo- and phyto-plankton, different trophic level of fish and seal samples have been studied for Hg speciation and Hg stable isotopes (Table). Also main ecological parameter and carbon/nitrogen stable isotopes were characterised for biological samples. Stable isotope Hg signature of LB plankton, fish and seal tissues showed positive correlation of $\delta^{202}\text{Hg}$ with trophic level. The comparison of the results obtained for contaminated and pristine sites suggests that Hg isotopic signature reveals both MeHg pathways in aquatic environments and trophic bioaccumulation routes.

Sample	[Hg] _{tot}	$\delta^{202}\text{Hg}$	$\Delta^{199}\text{Hg}$	%MeHg
Seal-muscle	300	+1.84‰	5.03‰	82.9‰
Perch(LB)	163	-0.48‰	1.14‰	95.1‰
Roach(LB)	58.6	-0.61‰	0.58‰	96.0‰
Plankton(LB)	2.1	-0.90‰	1.53‰	15.7‰
Pike(BWR)	3270	-0.18‰	0.04‰	90.6%
Perch(BWR)	1195	-0.26‰	0.52‰	92.0‰
Roach(BWR)	388	-0.17‰	1.19‰	94.2‰
Plankton(BWR)	3.6	-0.37‰	1.28‰	51.5‰

Table: Summarised total Hg (ng g⁻¹), MeHg content and isotope composition of Hg in some trophic web samples.

ICP-MS determination of trace elements in marine biological samples: Comparison of sample preparation procedures and selected digestion methods

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Marine biological samples (oysters, mussels, fish) can be used as bio-indicators to control the industrial pollution for the quality of aquatic environments and to investigate the toxicological impact for the different food chains. These samples with high sensitivity to toxic compounds in the surrounding water ecosystems are easily accessible resources that can be used for analysis.

Presented here is a comparison of two most used sample pretreatment techniques such as freeze-drying and fresh-freeze from the perspective of analytical efficiency and practical convenience of procedures applied to the processing of a considerable amount of samples. The concentrations of 20 elements in standard reference materials (SRMs) and different marine biological samples are studied and compared with previously published data. Validation of the pretreatment techniques are performed using several SRMs of oyster, fish and mussel tissues (1566b, 2977, TORT 2 and DORM 2) which display different matrix properties and large number of certified elements.

Lead cycling in forested catchments: Trends in input-output mass balances over 12 years of easing industrial pollution

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In Central Europe, forested headwater catchments are an important source of drinking water. In the second half of the 20th century, extensive coal mining and burning, along with chemical industry, metal smelting and traffic contributed to high emissions of a number of environmentally relevant elements. Lead (Pb) entering ecosystems via wet and dry deposition originated from all these sources. The highest anthropogenic emissions of Pb occurred in the mid 1980s, and a considerable decrease in Pb emissions has been observed over the past 25 years. The fate of lead and its potential release to stream water has been studied in 11 small spruce-forested catchments in the Czech Republic. Here we compare Pb input-output mass balances for the hydrological years 1996 and 2008, i.e., for periods of time 12 years apart. Atmospheric input via spruce canopy throughfall was monitored monthly. In clearings, two rain/snow collectors were installed per site. Stream discharge was sampled once a month near a gauging station. The calculated catchment-level Pb inputs have been vegetation-type weighted. In 1996, catchments situated in the more industrialized north of the country showed high Pb deposition rates of 25 to 50 g Pb ha⁻¹ yr⁻¹. Catchment situated in the less polluted south of the country showed lower Pb deposition rates of less than 17 g Pb ha⁻¹ yr⁻¹. Lead export via stream discharge formed less than 20 % of the input at most sites across the country. Only two sites in the industrial north (Krkonoše and Orlické Mts.) exhibited a higher proportion of exported Pb, relative to contemporary input (32 to 60 %). Overall, most of the anthropogenic Pb entering the ecosystems remained immobilized within the biomass and soils. Twelve years later, in 2008, atmospheric Pb depositions into all catchments significantly decreased, averaging 11 g Pb ha⁻¹ yr⁻¹. The amount of exported Pb, and the proportion of exported Pb, relative to contemporary atmospheric input, decreased in comparison with 1996. In 2008, the annual Pb export was less than 2 g ha⁻¹ yr⁻¹ at 8 out of 11 sites. Our data show that, with easing atmospheric pollution, less Pb is exported from the catchments, even though the total amount of Pb that had accumulated since the beginning of the Industrial Revolution (1860) was sizeable.

Biom mineralization and seawater dynamics in foraminifera studied with the fluorescent dye Calcein

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The calcite shells of foraminifera which accumulate on the ocean floor are an important component of the global carbon cycle. These shells provide highly valuable paleoceanographic information based on their trace elements and stable isotopes. Understanding their biom mineralization is therefore an essential goal both for ocean acidification studies and for obtaining new and reliable paleoceanographic information. Recently we showed that perforate foraminifera precipitate their calcite directly from seawater vacuoles [1, 2]. Here we describe the uptake and release dynamics of seawater in the benthic foraminifera *Amphistegina lobifera* and *A. lessoni* using pulse-chase experiments with the membrane impermeable fluorescent dye Calcein. Three different reservoirs of seawater stored in vacuoles were found with residence times of ~ 20 min., ~ 6 hr and ~ 10 days. The internal volume of seawater is large and it is recycled fast enough to provide Ca²⁺ and CO₃²⁻ for the normal calcification process. At low salinities Calcein released during the chase is higher than in normal salinity by a factor of 2. This may be part of the osmotic regulation mechanism in these giant cells. Calcein is incorporated into the shells in direct proportion to calcification measured by weight increase or by alkalinity depletion. The distribution coefficient of Calcein in the shells is very low in the order of 10⁻⁴. It increases significantly with salinity and with calcification rate and using Rayleigh type fractionation model we calculate that higher fraction of the calcification reservoir is utilized at optimal conditions. These observations provide the foundations for a realistic model to describe the behavior of stable isotopes and trace elements in the modified seawater calcification reservoir in foraminifera. Furthermore, it explains the sensitivity of foraminifera to ocean acidification.

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Using lead isotopes in marine barite to understand intermediate water dynamics

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Lead isotopes in marine barite hold the potential to provide insight into changes in intermediate water circulation. Marine barite forms at intermediate water depths and incorporates Pb into the crystal structure at ~2ppm. As a result, the isotopic composition of Pb in marine barite represents the ratios of dissolved Pb in intermediate water. The ability of marine barite to document this elusive water mass makes this new proxy a powerful tool in understanding intermediate water dynamics.

Since anthropogenic pollution has irrevocably altered Pb concentrations and isotope ratios in the present day ocean, calibration of Pb proxies relies on a survey of Holocene sources. We will present results from marine barite separated from several cores in the equatorial Pacific. The ferromanganese grain coatings and detrital fractions for many of these samples will also be presented. By analyzing these three fractions from the same sample, we show that marine barite is recording a unique signature. This implies that the Pb in intermediate water is different than that of deep water or the bulk detrital fraction, potentially allowing us to deconstruct dust and circulation based Pb sources.

Additional work documenting potential source regions for intermediate water lead will be presented. Preliminary box modeling work will be shown to help resolve these source questions and illustrate the unique utility of this emerging proxy.

Geochronological and thermochronological evolution of the southern Gaoligongshan metamorphic belt, Yunnan (China)

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The Gaoligongshan metamorphic belt is located east of the Eastern Himalayan Syntaxis (EHS) and plays a key role in the evolution of southeastern Tibet. Here, we present geochronological data of orthogneisses and mylonites that pertain to the evolution, cooling and exhumation history of this mountain range. Zircon U/Pb dating allow us to distinguish between at least four different magmatic events at about ~486 Ma, ~282 Ma, ~136 Ma and ~76 Ma. Similar ages have been reported for ortho-derivative rocks of the adjacent Tengchong and the Baoshan blocks and suggest that the southern Gaoligongshan is composed of rocks originally belonging to the Lhasa and the Sibumasu terrane derived rocks. Late Eocene to Early Miocene U-Pb zircon and Rb/Sr muscovite ages are coeval with the onset of lateral crustal displacement along major shear zones in Eastern Tibet and Indochina and post-collision volcanic activity in Western Yunnan. Main phase of crustal rotation in the Tengchong and Baoshan blocks and mylonitization along the Gaoligongshan shear zone started during the Miocene, between 19 and 12 Ma (Rb/Sr biotite and Ar/Ar mica ages). The final stage of exhumation of the Gaoligongshan is revealed by apatite FT and apatite (U-Th-Sm)/He thermochronology, with ages between 8 and 5 Ma, which was presumably triggered by crustal root delamination and backarc extensional processes as a consequence of the Andaman sea floor spreading.

Based on our results, we propose that the tectonometamorphic evolution of the Gaoligongshan was the result of Tibetan extrusion and escape tectonics around the EHS, the southeastward movement of Indochina and backarc-extensional effects of the Andaman seafloor spreading, which makes it to a junction point between Tibet Plateau and Indochina.

Building stone potential of the Eastern Black Sea Region, NE Turkey

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Turkey is located in the orogenic belt of the Alpin-Himalayan that has the world's richest natural stone formations. The country has rich marble and limestone formations on the one hand, travertine and onyx formations on the other hand. More than 500 natural stone sites, 800 factories operating in the sector and 90 % of the sites are located in the western Anatolia, mainly in Aegean and Marmara Region of Turkey. In all parts of Turkey, mainly Marmara and Aegean Region, there are good quality natural stone reserves. Although the eastern Black Sea region has limited number of natural stone variety it has a considerable number of natural stone reserves mainly granites. Total natural stone reserves are about 450 million tons and operated reserves were about one percent of this. However, there are more than 30 important natural stone sites in operation in the region. The reserve of the natural stones is about 13 million tons. The most important carbonate bearing marbles are travertines with the reserves of about 1.6 million meters cubes in total carbonate natural stones. In this study carbonate bearing natural stone potential of the eastern Black Sea region was revealed and their geological and geomechanical properties were investigated in terms of marbling sector.

Do melt inclusions record the pre-eruptive volatile content of magmas?

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In the last several decades the number of publications describing the use of melt inclusions (MI) to determine the pre-eruptive volatile contents of magmas has increased significantly. However, in most MI studies, the volatile contents of the MI within a single sample or even within a single phenocryst vary widely, and it is often not possible to assess the reliability of the data. In order for MI to provide reliable information concerning the pre-eruptive volatile content, the MI must obey Roedder's (Sorby's) Rules. Namely, the MI must have trapped a single homogeneous melt phase, the volume of the MI must remain constant after trapping, and nothing can be added or lost from the MI after trapping. The adherence to Roedder's Rules is tested by examining two or more melt inclusions from a Melt Inclusion Assemblage (MIA), representing a group of MI that were all trapped at the same time. If all of the MI in the assemblage show the same room temperature phase relations and the same composition, then it is highly likely that the MI in the assemblage obey Roedder's Rules.

In this study, the volatile contents of MI from well-characterized MIAs hosted in phenocrysts from White Island (New Zealand) and from Solchiaro (Italy) were analyzed by Secondary Ion Mass Spectrometry (SIMS). In some MIA, abundances of all of the volatiles (H₂O, F, Cl, CO₂ and S) were consistent in all MI within the MIA. In other MIAs, CO₂ and S abundances showed wide variation, with CO₂ most often showing large variability within an MIA. The reason for the wide range in CO₂ content is unknown, but could reflect small-scale heterogeneities in the melt during inclusion trapping or varying degrees of post-entrapment crystallization for MI in the MIA.

Mercury isotope fractionation during bio-accumulation in lichens

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Recently, mercury (Hg) isotope mass-independent fractionation (MIF) were reported in various lichens [1] and interpreted as the evidence for the atmospheric Hg to be a complementary reservoir to aquatic Hg [2] with respect to $\Delta^{199-201}\text{Hg}$. Recent data from the literature on more "direct" samples for atmospheric Hg [3, 4] suggest small Hg MIF, even slightly positive $\Delta^{199-201}\text{Hg}$, in contrast to significant negative $\Delta^{199-201}\text{Hg}$ values measured in lichens. This raised the question of the integrity of Hg isotopes measured in lichens relative to atmospheric matter, with the possibility of MIF during bio-accumulation.

A large amount of lichen tufts (*Evernia Prunastri*) was retrieved from trees in a small forest south of Nancy (France), rinsed with distilled water and dried at room temperature for a few days. Aliquots of bulk samples (1 g) were plunged into solutions (50 ml) containing various amounts of dissolved elements to simulate rain water. Lichens and solutions were in contact between 1 and 60 minutes (n=6).

Mass balance for Hg was calculated using Hg in lichens and Hg in the remaining solutions. Both were very similar suggesting that all Hg lost from the solution was pumped out by lichens (no wall adsorption). The $\delta^{202}\text{Hg}$ measured in lichens changed from -3.5‰ (initial value) to -0.5‰, interpreted as a progressive adsorption of solution Hg (0‰). However, Hg in the remaining solution shifted its $\delta^{202}\text{Hg}$ up to +1.5‰, decreasing with time, suggesting kinetic fractionation occurred when adsorption started. Isotopic equilibrium was not reached after 60% of total solution Hg was adsorbed by lichen ($\Delta^{202}\text{Hg}_{\text{sol-lichen}} \leq 1\text{‰}$).

Some lichens were exposed to sunlight (6 to 10 weeks) after being in contact with the NIST 3133 Hg, increasing their [Hg] variously from 0.15 to 18 $\mu\text{g/g}$. In all cases, no significant MIF were measured in both light exposed and non-exposed lichens, suggesting that bio-accumulation of Hg(II) by lichen do not result in MIF.

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Effect of initial Al concentration, pH and silicic acid on the formation and stability of tridecameric Al polymer

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Tridecameric Al polymer (the Keggin-type Al_{13} polycation)

Al^{3+} and its hydrolytic species which elute from soil due to the soil acidification have strongly toxic effect to plant and living organisms. In Al^{3+} hydrolytic species, tridecameric Al polymer (Keggin type Al_{13} polycation, $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$) show the strongest toxicity. Surprisingly, Hunter and Ross detected Al_{13} in organic horizon of forested Spodosol in USA [1]. Much attention has been paid to the formation conditions of Al_{13} . According to the equilibrium calculation, at the total Al concentration of 10^{-5} mol/dm³(M) which is the concentration level of soil solution, the occurrence of Al_{13} is sufficiently considered [2]. However, the detection of Al_{13} species such a low Al concentration is extremely difficult. Therefore, in this study, we developed the detection method of Al_{13} by ²⁷Al MAS NMR after adsorption onto chelate resin from solution with various Al concentration. Furthermore, we also studied the stability of Al_{13} on the solid surface and elution of Al species from solid surface and the effect of silicic acid to the formation and stability of Al_{13} .

When Al_{13} is formed in the soil environment, it is possible to adsorb on the surface of microbes and humic substances. In this study, the chelate resin was used as a model compound of the surface of microbes and humic substances because of similarity of functional group. For the concentration limit for the formation of Al_{13} , we could detect Al_{13} species after the adsorption onto chelate resin above 10^{-4} M. The pH range where Al_{13} can form in solution is very narrow [3], however, we also revealed that when Al_{13} adsorbed onto the resin, the pH range where it can exist clearly expanded. When the silicic acid coexisted in initial solution, the formation of Al_{13} distinguishably retarded.

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Stability and transformation of Pb smelter fly ash in soils

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Soils represent an important sink for metals released into the environment by anthropogenic activities. Emissions from non-ferrous metal smelters are responsible for extremely high concentrations of metals in adjacent soils related to the deposition of the fly ash particles during periods of the filtering inefficiency in the smelter flue-gas cleaning system [1, 2, 3].

To understand the dynamics and fate of smelter-derived contamination, we studied the reactivity of secondary Pb smelter fly ash in acidic soils. The polyamide bags (mesh 1 μm , 2 x 4 cm) were loaded with 0.5 g of fly ash and sealed by welding. Testing bags were placed in contrasting soils in two experiments: (i) a short-term (21-day) laboratory pot experiment with soil pore-water monitoring (Rhizon suction cups) and (ii) a long-term (1-year) *in situ* experiment in soils developed under different vegetation cover (spruce, beech, meadow). After each experiment, the bags were weighted to determine the mass loss and the weathered fly ash was studied by XRD and TEM/EDS. The total concentrations of metals, their chemical fractionation and Pb isotopic composition were determined in soils by the combination of ICP techniques.

More than 60% of fly ash was dissolved during the experiment, especially in organic soil horizons and secondary anglesite (PbSO_4) formed as a stable alteration product [1, 2]. A significant increase in the metal concentrations in the soils was observed during the experiment, especially in the litter and organic horizons: Cd (248 x), Pb (15 x), Zn (1.8 x). Cadmium was the most mobile element in the pots and soil profiles, being strongly released into the soil water and bound mostly in the labile soil fractions. A significant shift in the Pb isotopic values towards the fly ash signature ($^{206}\text{Pb}/^{207}\text{Pb} = 1.16$) confirmed the effect of smelter-induced contamination on metal dispersion, binding and mobility in soils.

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Treatment of rural effluents by infiltration percolation process using sand-clay fortified by pebbles

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Low-cost and high-performance decentralized wastewater treatments system for rural application in developing nations necessitated this study. The grain size and mineralogy of the sand filter constituting the infiltration bed, is of course one of the key elements and is the main subject of this article. In the other hand, clay samples collected from north eastern Tunisia were characterized by studying the mineralogical and geochemical composition and prove her great potential to fix pollutants. Performance efficiency studies were conducted to determine the best combination ratio of sand-clay/pebbles. Sand-clay (mixture contain 90% sand 10% of clay in weight) fortified with pebbles in the ratio 3:1 gave the optimum water purification and appropriate permeability for the infiltration percolation system. The effects of continued usage on the performance efficiency of the fortified column were studied and the results showed a decrease of Nitrogen, BOD, COD and Bacteria.

A possible evidence of urbanization effect on the light precipitation in the mid-Korean peninsula

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The continuous urbanization by a rapid economic growth and a steady increase in population could affect the meteorology in the downstream region [1]. This study presents the associated analysis of long-term (1972~2007) precipitation trends in the mid-Korean peninsula and the WRF model simulation for a golden day (2009/2/11). The mid-Korean peninsula has very favorable geographic characteristics for the study of urbanization effect on the cloud and precipitation in the downstream region such that Seoul metropolitan area is located in the west, with relatively flat area in the east, and the big mountains along the east coast. The analysis stations consist of the urban region (Seoul, Incheon, Suwon), its downwind region (Chuncheon, Wonju, Hongcheon), and the mountainous region (Daegwallyeong). The trend of population, as a surrogate of urbanization, continues to increase. The category of precipitation amount (PA) is divided by the intensity such as light precipitation for $PA \leq 1 \text{ mm d}^{-1}$, intermediate for $1 \text{ mm d}^{-1} < PA \leq 10 \text{ mm d}^{-1}$, and heavy for $PA > 10 \text{ mm d}^{-1}$, respectively.

During the long-term period, PA and PF (precipitation frequency) in the downwind region of urban area significantly increased for the westerly and light precipitation case only, while PA and PF in the mountainous region decreased. Especially the enhancement ratio of PA and PF for the downwind area vs. urban area remarkably increased, implying the possible urbanization effect on the downwind precipitation. In addition, the WRF simulation applied for a golden day demonstrates the enhanced convergence and its associated updraft in the downwind area (about 60 km from the urban), leading to an increase in the cloud mixing ratio.

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Polysaccharide fractionation of soil organic matter due to reaction with ferrihydrite

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Ferrihydrite, a poorly crystalline Fe oxyhydroxide, is known to be highly reactive towards soil organic matter (OM) and may play an important role in its long-term stabilization. To investigate composition and maximum OM loading of ferrihydrite-OM associations, we performed adsorption and coprecipitation experiments at pH 4.5 using the water-extractable OM of a Podzol forest-floor layer. The reaction products were studied by ¹³C CPMAS NMR, FTIR and analysis of hydrolyzable neutral polysaccharides. To better understand the behavior of polysaccharides, adsorption and coprecipitation experiments were also done with glucose, galactose and glucuronic acid.

Adsorption and coprecipitation of the forest-floor extract yielded similar maximum loadings of 195 and 170 mg C g⁻¹ ferrihydrite. Relative to the original forest-floor extract, the ferrihydrite-associated OM was enriched in polysaccharides, but depleted in aliphatic C and carbonyl C, especially when adsorption took place. Moreover, mannose and glucose were bound preferentially to ferrihydrite, while fucose, arabinose, xylose and galactose remained in the supernatant. This fractionation of sugar monomers was more pronounced during coprecipitation. Experiments with synthetic sugar monomers resulted in relatively low maximum loadings of ~15 and ~25 mg C g⁻¹ for glucose and galactose, whereas glucuronic acid produced a maximum loading of 72 mg C g⁻¹. Signals of ferrihydrite-associated glucose and galactose were hardly detectable by FTIR, whereas spectra of ferrihydrite-associated glucuronic acid closely resembled that of the ferrihydrite-associated forest-floor extract.

We conclude that the observed preferential association of polysaccharides from natural OM with ferrihydrite is not caused by direct interaction of the neutral polysaccharides' hydroxyls. Instead of that, we assume that (i) the dominant adsorption mechanism is outer-sphere complexation of carboxyls on the ferrihydrite surface and (ii) the enrichment of glucose and mannose in the ferrihydrite-associated OM may be explained by a preferential association of these monomers with carboxyl-rich compounds.

An Eocene analogue for the future oceanic response to increased CO₂ – Existence of a tropical thermostat?

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Future anthropogenic-induced atmospheric greenhouse gas increase is expected to result in a globally warmer Earth. Whilst this will likely result in an increase of high-latitude sea surface temperatures (SST), the future response of the tropical oceans is uncertain. It has been suggested [1] that a tropical 'thermostat' regulates low-latitude surface ocean temperatures. The mid-Eocene was characterised by higher atmospheric greenhouse gas concentrations [2] and therefore may provide a suitable analogue with which to test the thermostat hypothesis. However, there is disagreement between different palaeo-temperature proxies and recent climate models, with some suggesting considerably warmer Eocene SST.

We present new Eocene tropical ocean surface temperature data from central Java, based on a calibration of the relationship between test Mg/Ca and temperature in large benthic foraminifera. This is the first time such material has been used for palaeo-temperature reconstructions, including appropriate corrections for both changes in the ionic composition of seawater over geological time and corresponding D_{Mg} variation. Large benthic foraminifera were chosen over their more routinely studied planktic relatives because they are longer lived and therefore facilitate both annual and seasonal temperature reconstruction. This is important because it is now recognised that seasonality is a key component of climate change [3].

Our results, measured by laser-ablation plasma mass spectrometry, indicate Eocene southeast Asia tropical SST broadly similar to today. These data, backed by a compilation of δ¹⁸O-derived temperatures from well-preserved planktic foraminifera, support the existence of a tropical thermostat. Moreover, comparison with higher palaeo-latitude LBF from the Hampshire Basin (UK) provides further evidence that oceanic latitudinal temperature gradients were greatly reduced when compared to the present day.

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What can equilibrium thermodynamics tell us about metasomatic alteration?

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In metamorphic petrology, equilibrium thermodynamics is often used to help us interpret metamorphic evolution of rocks that, we can reasonably assume, evolved close to thermodynamic equilibrium, with a relatively fixed bulk composition, except for volatiles, and under conditions where pressure and temperature are controlling intensive variables.

In rocks that have been significantly affected by metasomatic alteration, these assumptions are, in many cases, no longer reasonable. The nature of a metasomatic rock means that chemical potential variables are likely to have been fixed during their formation, rather than bulk composition variables. Metasomatic processes can also happen quickly, so the assumption of thermodynamic equilibrium on all but the shortest length scales might be faulty. Further, the changes in volume may be sufficient that it might be appropriate to consider volume, rather than pressure as a controlling variable.

Such observations are not new, but they are worth revisiting in the light of the massive recent improvements in imaging and analytical techniques that have led to renewed appreciation of the importance of processes such as dissolution-precipitation, and an increased understanding of the mechanics of metasomatic alteration.

Here, methods to improve the conceptual models and quantification of metasomatism, are discussed. These include judicious use of the phase rule, appropriate choices of conjugate variables, and methods to assess the lengthscales over which thermodynamic equilibrium may have applied. These methods are discussed with reference to metasomatic alteration of BIF-derived iron ore and serpentinisation of ultramafic rocks.

The relationship between subduction zone redox budget and arc magma fertility

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A number of lines of evidence point to a causal link between oxidised slab-derived fluids, oxidised sub-arc mantle, and the formation of economic concentrations of metals such as Cu and Au that require oxidised magmas. However, trace element evidence from V/Sc ratios suggests that sub-arc mantle is no more oxidised than mantle elsewhere.

A simple analytical model is applied to constrain the evolution of sub-arc mantle oxidation state as a function of redox-budget fluxes from the subducting slab. Influential variables include the solubility of Fe³⁺ and SO₄²⁻ in slab-derived fluids, the geometry of the infiltration of slab-derived fluids in sub-arc mantle, the coupling between slab-derived and arc-output redox budgets, and the concentration of redox-buffering elements such as Fe and S in the sub-arc mantle.

Plausible Archean and Proterozoic redox budget fluxes would not have created oxidised sub-arc mantle. Phanerozoic redox budget fluxes, on the other hand, which are dominated by the sulfate component, could have increased sub-arc fO_2 by up to three log₁₀ units. The results are generally consistent with the proposed elevated fO_2 for sub-arc mantle but do not explain V/Sc results.

Increases in sub-arc mantle fO_2 are favoured by focussed fluid infiltration and magma generation, weak coupling between slab and arc-output redox budgets, and restricted redox-buffering in the sub-arc mantle. Fertile arc segments for ore deposits associated with oxidised magmas require fluid chemistry and pressure-temperature gradients that enhance Fe³⁺ and SO₄²⁻ solubility in aqueous and silica-rich fluids, tectonic stress regimes that favour focussed transfer of components into the sub-arc mantle, and a relatively weak redox buffer for the sub-arc mantle. The paucity of Cu and Au deposits associated with oxidised magmas in the Precambrian may be explained as a consequence of a lack of subducted oxidised material, rather than simply as a consequence of preservation potential. Additionally, the reduced nature of subducted material in the Precambrian may have caused S and metal enrichment in the sub-arc mantle.

Coffinitization of uraninite – A review and discussion of observations on different scales

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Coffinite (USiO₄•nH₂O) is a common secondary mineral in uranium ores, observed to replace uraninite in response to alteration of uraninite in a reducing environment [1]. This process is often referred to as coffinitization. However, it has proven difficult to synthesize coffinite in the laboratory, and in nature, coffinite is commonly very finegrained, resulting in a lack of experimental data concerning thermodynamic properties for coffinite [2,3]. As is noted by [2], there are natural, coarse-grained coffinite crystals available from the Grants uranium region. However, it is also observed by [4] that there exists intermediate solid solutions in the system thorite–xenotime–zircon–coffinite and that in natural samples, moderate to strong deviation from perfect stoichiometry is commonplace.

In a recent attempt to synthesize coffinite [3], aqueous U was added to a Si-rich solution under controlled conditions to form a green gel subsequently heated for a few days in condition-controlled autoclave. This produced coffinite but only as a nanocrystalline mixture between coffinite and UO₂. Another experiment investigated the hydrothermal alteration of pellets of UO₂ in groundwater spiked with CaCl₂, NaHCO₃ and Na₂SiO₃[5]. At the end of the experiment (180 °C, c. 40 days, reducing environment) about 25% of the pellet surface was covered with a phase with a U:Si element ratio of 1:1. However, it was not possible to identify this material as coffinite by XRD.

In spite of these experimental difficulties, coffinite is a widespread alteration product of uraninite. This review aims to elucidate the spatial relationships between coffinite and uraninite as seen on different scales with different methods. The mechanism of uraninite alteration in natural, reducing, Si-rich environments is discussed and some new arguments put forward, involving the effect of impurities, defects, and grain size. Coffinitization is discussed in terms of solid-fluid interaction.

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Tin substitution in chalcopyrite and sphalerite from hydrothermal sulfides

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Unusual tin concentrations (500-2000ppm) were measured in sulfides from the Logatchev hydrothermal field. This hydrothermal site is located on the Mid-Atlantic Ridge, at a depth of 3000 m in an ultramafic environment. The fluid temperature was measured between 300 and 350°C at the exit of the chimneys.

Tin is usually not present in marine sulfides, but detailed microprobe and SEM analyses and element mapping showed a specific distribution for this metal. High tin concentration, are mostly in sphalerite (3 to 5%wt) and chalcopyrite (1 to 2%wt) from the hot part of the chimneys. The highest concentrations, up to 6%wt, are located at the replacement front of chalcopyrite and sphalerite.

Raman spectroscopy studies exclude the presence of tin minerals, like stannite, kesterite or cassiterite, and prove that tin is substituted in the lattice of sphalerite or of chalcopyrite.

The variation of the fluid composition, the temperature and the pressure induces the evolution of the chimney and changes in its mineral composition. These changes, linked to substitution, create different types of minerals with different valence, like $\text{Cu}^+\text{Fe}^{3+}\text{S}^{2-}_2$ and $\text{Cu}^{2+}\text{Fe}^{2+}\text{S}^{2-}_2$ for chalcopyrite.

Fe^{2+} is oxidized in Fe^{3+} at high temperature in spite of the oxygen free environment [1] and enhance the tin substitution with the reaction: $2\text{Fe}^{3+} \leftrightarrow \text{Sn}^{4+}\text{Fe}^{2+}$ [2].

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Interesting finds in Norilsk copper-nickel sulfide ores

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Norilsk ores contain a unique set of ore minerals among which the minerals of platinum metals have a significant place. Nowadays more than 100 PGM are described in Noril'sk ores. Along with PGM the wide range of the rare minerals, considered unusual to deposits of similar type, is discovered in these ores. During detailed research using SEM+EDD some new data about PGM paragenesis, associated ore minerals, and unexpected mineral finds are obtained.

An investigation of massive copper rich sulfide ores with chalcopyrite group minerals (talnakhite, mooihoekite, putoranite) has shown, that fine-filiform band of copper sulfides, $\text{Cu}_2\text{S}/\text{Cu}_{2-x}\text{S}$, are often observed along PGM and sulfide mineral boundaries. The thickness of these bands generally does not exceed 0.n microns ($n \sim 2-5$). It could be the reason for some copper "surplus" in PGM composition.

Such observation could also explain the stoichiometry deviation observed on occasion in chalcopyrite group minerals. So, some sample compositions are enriched in Cu. It causes to "strange" formula with higher Cu apfu.

Beside sulfides (i.e. $\text{Ni}_{8\text{s}}$) among interesting minerals discovered recently in Cu-Ni-sulfide ores it possible to mention just a few: submicro- and nano-dimensional segregations of thorium, uranium and REE minerals - thorite, uranothorianite, Th-monacite, etc. The grain size of these minerals does not exceed a fraction of a micron. They are found in pyrrhotite ores, Oktyabrsky mine. It is necessary to note that in Taïmyr peninsula there is an uranium manifestation, named Kamenskoje. Now it is difficult to understand if there is any association of this manifestation with Cu-Fe-Ni-PGE deposits of Noril'sk region. But the finding of Pd-minerals in natural reactor Oklo, in U-bearing black shales, and some other information about "coexisting" PGE and U (Th) in nature allow one to discuss some genetic problems.

Insights into lower crustal evolution from Hf isotope and Zr thermometry data for rutile

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Chemical and isotopic analysis of minerals previously resident deep in the crust provides critical information towards understanding the formation, evolution and differentiation of the continental crust. Rutile is an accessory mineral in many lower crustal metapelites and is an appealing target for such studies, but its full potential has not yet been exploited. While the ability to measure Hf isotopes in rutile has been demonstrated [1], an understanding of the behaviour of this system in rutile at high temperatures is lacking. Hf isotope information for this mineral can be combined with temperatures determined by Zr-in-rutile thermometry.

In this study, the classic lower crustal section of the Ivrea-Verbanò Zone (IVZ), Italy, was used as a natural laboratory in which to explore the behaviour of the Hf isotope and Zr thermometry systems in rutile at high temperatures. Zr-in-rutile thermometry for a suite of granulite facies metapelites from the IVZ records high temperatures related to peak metamorphic conditions, as well as resetting of the Zr-in-rutile thermometer in some grains. Rutile from metapelite slivers incorporated into the underplating Mafic Complex record heating to temperatures in excess of 1000 °C during emplacement of the gabbro. Zr-in-rutile is the only thermometer to record this extreme thermal overprint, which is not recorded by Ti-in-zircon or Fe-Mg thermometry.

Hf isotope data for the same suite of metapelites demonstrate that rutile preserves a robust record of Hf isotope composition, even under conditions of high temperature metamorphism and partial melting. The results also demonstrate that in metapelites that have experienced the highest temperatures, zircon dissolution plays an important role in determining the Hf isotope composition of subsequently-formed phases. This observation has profound implications for the interpretation of Hf isotope data for all minerals in both metamorphic and magmatic systems. When complete dissolution of zircon occurs, rutile is shown to become the main host of Zr and Hf in these samples, and controls the Zr/Hf of residue and melt.

The new results demonstrate the valuable contribution that chemical and isotopic analysis of rutile can make to constraining the evolution of the lower crust.

[1] Ewing *et al.* (2011) *Chem. Geol.* **281**, 72-82.