Neoproterozoic accretion along the southeastern margin of the Eastern Dharwar Craton, India: Evidence from zircon U-Pb ages and their Hf isotopic composition

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Late Mesoproterozoic high-grade tectonothermal event due to collision of the Eastern Ghats Belt [1] with the Eastern Dharwar-Bastar Cratons, is not recorded by the Paleoproterozoic Krishna Province rocks [2] south of the Godavari graben [3]. The Vinjamuru domain represents Paleoproterozoic metaigneous rocks of a continental arc accreted to the margin of the Eastern Dharwar Craton [4] and coeval with the UHT granulite-facies event in the easternmost Ongole domain [2]. Here, we report zircon isotopic data from one critical amphibolite-facies metaandesite sample (VL47) from the central Vinjamuru domain.

The U-Pb zircon ages in this metavolcanic rock record a protracted polycyclic evolutionary history (Fig.1). Derivation of youngest zircons from crustal melts are seen in their negative $\varepsilon_{Hf(t)}$ values at two clusters: $907-1111$ Ma ($\varepsilon_{Hf(t)} = -5$ to -7) and $696-810$ Ma ($\varepsilon_{Hf(t)} = -21$ to -9). The most likely interpretation of our data is that the Vinjamuru domain rocks also record latest Neoproterozoic accretion (and coeval metamorphism) of the Ongole domain to the Vinjamuru domain, supporting one interpretation of this Eastern Ghats-craton collision at 820 Ma [5].

Role of Bacillus mucilaginosus at silicon biogeochemical cycle in a system “soil – plant”

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Silicate bacteria Bacillus mucilaginosus B-1574 were studied at four steps. First we demonstrated direct evidences that this strain has geochemical activity and is able to leach $Si$ and $P$ from the object of lithosphere - phosphoric ore of Djerioi mining in Uzbekistan, %: $P_2O_5$-13,6; $CaO$-44,75; $MgO$-1,05; $CO_2$-20,88; $Fe_2O_3$-3,03; $SiO_2$-2,7; $C_{org}$-0,11 (Fig.1, Table 1).

Bacteria of natural biocenosis from Tomsk grey forest soil Bacillus mucilaginosus strain B-1574

Figure 1: SEM-photos of fragments of a surface of rock particles after 30-days incubation with bacteria, x5000

Table 1: Transfer of silicon and phosphorus into a solution

<table>
<thead>
<tr>
<th>Days</th>
<th>$N$ bacteria, $x10^9$, cell/ml</th>
<th>$SiO_2$, mg/l</th>
<th>$PO_4^{3-}$, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.00021</td>
<td>5.62</td>
<td>4.75</td>
</tr>
<tr>
<td>10</td>
<td>0.05</td>
<td>6.62</td>
<td>5.25</td>
</tr>
<tr>
<td>30</td>
<td>0.12</td>
<td>20.0</td>
<td>6.38</td>
</tr>
</tbody>
</table>

Table 1: Transfer of silicon and phosphorus into a solution

Then we revealed in a liquid culture of this strain significant amounts of organic and ketoacids, polysaccharides, IAA, three individual cytokinins. At the third step we made experiments with mineral “Vermiculite” as a model of secondary aluminosilicates. 60 elements were detected in a supernatant by ICP-MS after 50-days incubation with bacteria. Control/Treatment, mg/ml: Mg-84/388; Al- 0.078/2500; Si-26/98; Ca-122/238; Cr-0.054/0.250; Mn- 0.085/3.41; Fe-1.61/36.4; Co-0.015/0.056; Cu- 0.12/0.17; Zn- 0.061/0.390; Mo-0.020/0.031. Then we measured mono-, polysilicic acids and Si-organic compounds in grey forest soil, urbozem and in plants. In both soils we grew Triticum aestivum L., Cucumis sativus L.: soil polysilicic acids after bacteria activity are the source of plant biolites.
The first data about the REE’s contents in new-formed phases (Berezitovoe gold deposit, Priamurye, Russia)

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Here we present the first data on contents and geochemistry of REEs in the secondary new-formed phases from weathering zone of Beresitovy gold deposit hostrocks. Also the analysis of fractionation and migration of REE in single geochemical cycle “bedrock - weathering zone - surface and ground water - secondary new-formed phases” are performed.

The Beresitovy gold deposit located in the northeastern Amur gold province in the downstream basin of the Khaikta River. In 2007, two mining companies: Berezitovy Mine Ltd. and High River Gold Mines Ltd., started to mine this deposit. Geologically, the deposit is localized in a southeast part of the North Asian craton, in a zone of its joint with formations of northern frame Tukuringra-Dzhagdinsky terrein Mongolo-Ohotsky zone. Two formations of sediments (granites and ore–metasomatic rocks) occur in the deposit. Main minerals bearing REEs are allanit, monatsit -(Ce), chervandonit -(Ce).

The preliminarily results of investigation showed, that the content and distribution of REEs in the new-formed phases from weathering zone of deposit. Our data indicate that the content of REEs in new-formed phases of Berezitovoe deposit can reach up to 149 ppm and the content of LREEs is at about 93% of total REEs. All types of new-formed phases display of strong negative Ce and Nd anomalies.

Profiles of distribution of REE of new-formed phases are comparable to bedrock profiles, small difference is observed in distribution heavy groups of elements.

Relation between diatom communities and the degree of AMD affection in selected water dams in Iberian Pyrite Belt

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In mining regions the presence of water reservoirs affected by AMD is a common problem. This study is part of a project that characterizes the water dams in the Spanish Iberian Pyrite Belt, in order to achieve a classification based on the effects by AMD. This preliminary work presents data from four selected dams: mining dams (Gossan and Águas Ácidas), for industrial use (Sancho), and for human supply (Andévalo). The main objectives are: i) to describe the water and sediment properties; ii) to characterize diatom communities, and iii) to find possible relations between diatoms and the degree of AMD. Chemical composition of water and sediments was determined by AAS and ICP-MS. XRD was performed for mineralogy (bulk and clay fractions). Diatoms were sampled from sediments. Identification and quantification were performed in slides mounted with Naphrax®. Results indicate that the four dams are subject to the effect of metallic loads from polluted rivers, although with different levels: Águas Ácidas>Gossan>Sancho>Andévalo. In accordance, diatom communities have differences in composition and dominant diatom taxa. *Pinnularia acidophila* and *P. aljustrelica* were found dominant in the most acidic dams (Gossan and Águas Ácidas), *Pinnularia subcapitata* was dominant in Sancho and *Eunotia exigua* in Andévalo.
Zirconology of UHP-ultramafic rocks and eclogites from the Maksyutovo complex (South Urals, Russia)

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The U-Pb SHRIMP age of zircons was specified for the UHP-ultramafic rocks (Fo+En+Mgs+Ti-Chu) and jadeite eclogites (Jd+Grs-Alm+Rt+Pb) from the Maksyutovo eclogite-glaucophane schist complex.

The zircon age comprise a range of more than 2 Ga. The most ancient age of 2350±35 Ma corresponds to the primary mantle protolith. The ages of 1644±10, 1492±16 and 1294±64 Ma characterize the different stages of evolution of this mantle protolithe.

The Lower Cambrian age of the most crystals from ultramafic rock and eclogite is similar (545.3±5.8 Ma [1] and 533±4.6, respectively). The validity of this age is confirmed by variations of U (113–332 ppm) and Th (41–281 ppm) contents and U/Th ratio (0.43–0.92) that corresponds to the age of the UHP-metamorphism (P ≈ 4.4 GPa, T ≈ 700 °C).

The ultramafic rocks and jadeite eclogites represent the UHP metamorphized tectonic mantle-crustal blocks in quartzite-shists of the first unit of the complex.

Fig.1 The U-Pb age of zircons from jadeite eclogite.

The Late Devonian (365.3±4.2–360±3 Ma) is the next important stage in the evolution of zircons and rocks. This zircon group is significantly distinct in U content and are characterized by typically magmatic U and Th distribution, which may be interpreted as an index of the progressive stage of HP-metamorphism (P ≈ 1.1–2.2 GPa, T ≈ 450–550 °C). This stage of HP-metamorphism is manifested in all rock associations from the first unit of this complex.

The Early Permian last stage (284.9±7.3 Ma), recording the final transformations of previous generations and appearance of newly formed zircon, was caused by the late shear deformations.

Tomography at Single-Atom Scale of $^{207}$Pb and $^{206}$Pb in a 4374 Ma Zircon


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Local-Electrode Atom Probe (LEAP) tomography can identify and determine the position (±0.2nm) of individual atoms in minerals. These data allow 3-D observations at an unprecedented scale, including new insights on thermal history, radiation damage and element mobility in zircon. “Needles” were milled by FIB (~150nm dia. x ~1µm) and analysed by LEAP from the 4374 Ma core of a zircon from the Jack Hills, WA that has a 3400 Ma magmatic rim. In 3-D, Pb & YREE are co-localized and concentrated in ~5nm clusters, spaced ~20-50nm apart. The $^{207}$Pb/$^{206}$Pb ratios (7/6) by LEAP average: 1.23±0.11 inside clusters, 0.32±0.10 outside clusters, and 0.52±0.08 for the full volume of 2 needles (0.04µm³, 6x10⁸ ions detected). Significant $^{204}$Pb is not detected. U appears homogeneously distributed. Thus Pb in clusters is radiogenic and unsupported by U. LEAP data for other zircons (Valley et al. 2012 AGU) suggest that Pb &YREE were concentrated in clusters by diffusion into nanodomains of α-recoil damage. Diffusion distances of ~20nm for these elements in crystalline zircon require temperatures >700°C. In the 4374 Ma zircon, 7/6 by SIMS is 0.5476 in the core and 0.2912 in the rim (3400 Ma) in agreement with LEAP. A model age for LEAP 7/6 =1.23 in clusters would be older than Earth; however, diffusion during magmatic heating at 3400 Ma (rim age) could produce unsupported Pb clusters with (7/6)Δt age of 1.20. Thus, LEAP uniquely explains closed system behavior at the 20-µm-scale of SIMS while documenting Pb mobility at nm-scale. These results refute challenges (based on Pb mobility) to the accuracy of SIMS analyses of age for zircons with similar history and confirm the existence of a population of ~4.4 Ga zircons from the early Earth.

Rhenium-osmium dating of Mississippi-Valley-Type ore deposits: The Robb Lake Pb-Zn deposit, British Columbia

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Mississippi-Valley-Type (MVT) ore deposits are formed by fluid flow in sedimentary basins and comprise a large portion of global Pb-Zn resources. Dating the formation of MVT deposits has been attempted by dating their host rocks (Sm-Nd, U-Pb), paleomagnetic measurements or Rb-Sr dating of sphalerite, but all of these methods and results remain inconclusive and controversial to some degree. Pyrite as a major phase in MVT deposits can be dated directly using the long-lived Re-Os isotope system, which has been established to date sulfide formation.

The Robb Lake Pb-Zn deposit in northeastern B.C. is hosted by Silurian-Devonian platform carbonates, and forms part of a sequence of MVT deposits in the northern Rocky Mountains. The timing of its formation is still subject to controversy as two groups of ages are commonly cited. On the one hand, sulfide-forming fluid flow is considered to be associated with the Late Devonian - Early Carboniferous Antler orogeny, based on Rb-Sr studies, fluid inclusion composition, stable isotope data, and ages from other western Canadian MVT deposits along the Presqu’ile Barrier (Pine Point, NWT, [1]). On the other hand, Laramide (~65 Ma) ages have been suggested based on numerical modeling of regional fluid flow and paleomagnetism [2].

The Re-Os systematics of pyrite from Robb Lake are quite complex with substantial Re-Os being contained in both the pyrite and the associated dolomite breccia. Leaching of the dolomite using HCl allows for a more reliable age to be calculated from pyrite. A Re-Os isochron for this leached pyrite yields an age of 331 ± 40 (MSWD = 151). Identifying and removing data points that likely still have dolomite contamination produces an age of 351 ± 35 (MSWD = 18). The Re-Os data, although complex, confirm a Carboniferous age for sulfide formation associated with the Antler Orogeny.

Study of the natural iron fertilization off Crozet and Kerguelen Islands (Southern Ocean) using radium isotopes as tracers

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The Southern Ocean is known as the largest High-Nutrient, Low-Chlorophyll (HNLC) region of the global ocean. Phytoplankton blooms, however, take place annually off islands and associated plateaus that constitute physical barriers for the Antarctic Circumpolar Current. These phytoplankton blooms were shown to be sustained by natural iron fertilization associated with these topographic features. In the framework of the KEOPS-2 project, we used radium isotopes (Ra) as tracers of iron sources that fuel the phytoplankton blooms around Crozet and Kerguelen Islands, following previous works by [Charette et al., 2007] and [van Beek et al., 2008], respectively. In this work, we report one of the few studies that analyzed all four radium isotopes (224Ra, 223Ra, 228Ra, 226Ra) in Southern Ocean waters. Ra isotopes were used i) to trace the input of iron - and other micronutrients - released by the sediments deposited onto the margins and that sustain phytoplankton blooms, ii) to investigate the pathways of the waters that fuel the phytoplankton bloom north of Crozet Islands and east of Kerguelen Island, and iii) to estimate “apparent ages” for offshore waters. When combined to physical observations and modeling, information provided by our geochemical tracers allows us to assess the rates and timescales of the exchange between the islands and offshore waters and to give information on the origin and mechanism of iron fertilization in these areas.

Ocean ridge magma generation rates at slow-spreading ridges favour Hess-type oceanic crust

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The widely accepted model for the structure and composition of oceanic crust is based on the ‘Steinmann Trinity’ or Penrose ophiolite stratigraphy. This has an oceanic crust of mafic rocks: basalt pillow lavas with their feeder dykes (sheeted dyke complex) and gabbro plutons, underlain by the ultramafic, peridotite mantle. However, recent work on slow-spreading ridge systems has revealed significant deviations from this simple layered structure[1,2,3]. The thickness of the oceanic crust is derived from geophysical data interpretations assuming that the crust is wholly mafic but a melange of partly serpentinised mantle peridotite and mafic rocks can equally fit the data. If it is accepted that the crust is not completely mafic, then constraints on the amount of generated mafic magma have to be derived elsewhere. The amount of generated magma is determined by the melt generation rate and time, and by the volume of the melt zone.

We have derived melt generation rates for peridotite melting in the garnet stability zone between depths of the solidus at130Km and 95Km by modelling our U-series data for basaltic glass samples collected by ROV from the Mid Atlantic Ridge slow-spreading centre at 45ºN. Our results can be expanded with published results from thermodynamic modelling to estimate total decompression melt generation. We assume that the volume of the melt zone is given by the width of the active volcanicity in the median valley and the depth to the solidus, with 1Km along strike as the distance over which volcanic and tectonic characteristics can be considered as representative. We argue that in an area of tectonic extension, magma ascends vertically and is not focussed.

The our derived magma flux at ‘normal’ slow-spreading ridge segments, contributes <50% of the volume of crust, the remainder probably is serpentinised mantle peridotite. These inferences are agreement with the ‘Hess’ model for oceanic crust.

Soil Respiration – A Wetlands Perspective

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Wetlands are an essential part of the Earth’s life support system. They provide a wide range of ecosystem services, from food production, via flood protection to pollution abatement. In many parts of the world, however, mounting anthropogenic pressures, for example, water diversion, encroachment, salinization and climate change, are threatening wetlands. Because of their significance, as well as their vulnerability, wetlands are the only class of ecosystems with an international convention dedicated to their protection and sustainable use (the Ramsar Convention). In this presentation I will focus on the biogeochemical functions of wetland soils. As soil biogeochemistry is largely driven by the decomposition of plant-derived organic matter by microorganisms, I will review a number of the physical, biological and geochemical factors that control the turnover of organic matter in wetland soils. Besides the nature of the organic matter itself, key controlling factors include the soil pore network, soil aggregation, water saturation, redox conditions, temperature, and the microbial community structure. I will further discuss the importance of bioenergetic limitations on soil respiration processes. To conclude the presentation, I will highlight a number of areas where I believe geochemists can provide new and timely insights, for example on the effects of redox fluctuations and freeze–thaw cycles on soil organic matter decomposition.

Where Groundwater Meets Surface Water

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Biogeochemical processes at transitions between groundwater and surface waters play a major role in the regional biogeochemical cycles of carbon, nutrients and trace elements. These interfaces occur along the entire aquatic continuum, from headwaters to the coastal zone, and include flood plains, seepage areas, riparian soils and the hyporheic zone. However, while the biogeochemical significance of groundwater–surface water interfaces (GSWIs) is generally recognized, the underlying mechanisms and determining properties have yet to be fully unravelled. GSWIs exhibit unique hydrological, geochemical and ecological characteristics, including variable hydraulic gradients, complex flow dynamics, fluctuating redox conditions and diverse, multifunctional biological communities. In this presentation, I will highlight the biogeochemical functions of GSWIs, with a particular emphasis on the biogeochemical implications of the dynamic redox conditions that characterize many GSWI environments. The key take-home message of the presentation is that observations made under stable, “average” environmental conditions may not be sufficient to predict the fate of nutrients and contaminants at GSWIs. Stated otherwise, rate measurements, chemical speciation, microbial abundance, biodiversity, and other experimental data should be obtained under the dynamic conditions representative of GSWIs, both in the laboratory and in the field.
The oceanic cycles of the transition metals and their isotopes

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The transition metals show variable behaviour in the oceans, from the conservative but redox-dependent behaviour of Mo, through control by scavenging for Cu, to clearly biologically cycled elements like Ni and Zn. Thus, the abundances of these elements in ocean sediments have been used to understand temporal variability in a variety of key parameters for ocean biogeochemistry. Their isotopic systems are also often now available for study, but much remains to be done to understand the important processes fractionating the isotope systems. Here we assess their oceanic mass balance from an elemental and isotopic perspective.

A common feature of all the elements considered here (Mo, Zn, Cu, Ni) is the fact that the dissolved riverine input to the oceans is isotopically heavier than the continental crust, requiring isotopic fractionation during weathering and riverine transport. Moreover, the oceanic dissolved pool is, in all cases, heavier still. For example, the dissolved phase in rivers has δ60Ni ~0.8‰, versus silicate rocks at around +0.1 to +0.2 ‰. The dissolved pool in the oceans has δ60Ni = +1.44±0.15‰. Such isotopic data, for Ni and other metals, impose significant constraints on the marine budgets of these elements. There must, for example, be at least one isotopically light sink that renders seawater heavy.

Our approach to elemental mass balance has been to couple the size of the better-known Mo sinks with their metal/Mo ratios. For Cu and Zn the total known outputs are of the same order as, but slightly smaller than, the dissolved riverine input. However, the same approach with Ni highlights a major problem: the output of Ni to Fe-Mn oxides (isotopically close to seawater [1]) is close to an order of magnitude greater than the dissolved riverine input, a finding that is also made for Mn. This imbalance requires a large input for these two elements that is not significant for Mo. One possibility, given the high Ni/Mo and Mn/Mo ratios of riverine suspended load, is that both these elements are mobilised by reduction of oxide coatings in anoxic sediments in estuaries. But either these coatings are isotopically heavy or such a proposal would make simultaneous balancing of the oceanic elemental and isotopic mass budgets impossible.

[1] Gall et al. (submitted) EPSL.

Isotopic Fingerprint of Ice-Rafted Debris from the Antarctic Margin: A Spatial Record of Initial Ice Growth

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The onset of widespread Antarctic glaciation across the Eocene-Oligocene transition (~34 Ma) marks one of the most fundamental climate shifts in recent Earth history representing a major step from the greenhouse world of the Cretaceous and early Cenozoic to the icehouse world of today. State-of-the-art climate models suggest that ice expansion initiated at high elevation nucleation points in response to declining atmospheric carbon dioxide concentrations. While marine oxygen isotope records indicate a very rapid ice growth across the Eocene-Oligocene transition, models differ as to which parts of the continent were actually ice covered during the first extensive pulse of glaciation. Such knowledge however may be crucial for understanding important carbon cycle feedbacks in the Southern Ocean.

Here we investigate the geochemical fingerprint of early Oligocene ice-rafted debris (IRD) layers at two locations off East Antarctica: ODP Site 738 (Kerguelen Plateau) and IODP Site U1356 (Adélie Coast). 40Ar/39Ar ages of ice-rafted hornblende grains (>150 µm) reveal the tectono-metamorphic age of the grains, and hence provide a way to constrain spatial distribution of the initial ice surges. The first peak of IRD on the Kerguelen Plateau is well characterised and shows a clear Pan-African provenance, with 40Ar/39Ar hornblende ages of ~520 Ma, pointing to an origin from the nearby Prydz Bay sector. In contrast, one of the first prominent Oligocene IRD layers offshore the Adélie Coast reveals 40Ar/39Ar hornblende ages of ~1500 Ma. Such ages indicate provenance from the local Mertz Shear Zone. We will discuss details of our new data set in the context of model results on initial ice expansion and potential Southern Ocean feedbacks.

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Novel method to reconstruct paleopressure: a combined clumped isotope and fluid inclusion technique

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Reconstructing the pressure conditions under which diagenetic minerals were precipitated in subsurface can not only enhance our understanding about the burial and diagenetic history of studied rocks, but also bring insight into fundamental processes of mineral precipitation. This novel method is thus relevant for both industrial applications, such as reservoir characterization, as for fundamental research.

We have investigated several carbonate samples from Spain and Oman using both the clumped isotope and the fluid inclusion methods. Clumped isotopes can be used as a paleothermometer, providing a temperature of precipitation of a mineral independent of the stable oxygen isotopic composition of the parent fluid. Hence, both temperature and the stable oxygen isotopic composition of the fluid from which the mineral precipitated are extracted from clumped isotope analysis. The fluid inclusion technique, which is a common technique that has been used for decades, also provides an estimate of the precipitation temperature of a mineral, in addition to information on fluid chemistry and salinity. The estimation of the precipitation temperature of a mineral in this method is based on the temperature of homogenization during cooling-heating experiments. This homogenization temperature is measured at the equilibrium stage between the fluid and the gas bubble. However, at the time of trapping, usually a homogeneous fluid is trapped (and this is a requisite for deriving reliable homogenization temperatures) and a difference between the homogenization and the trapping temperature is expected because of the pressure at trapping conditions and the compressibility of the fluid. Isochores that can be reconstructed based on the density of the fluids, derived from fluid inclusion measurements, can then be combined with the independent temperature data from clumped isotopes, so that both the temperature and pressure conditions during precipitation of the analysed mineral can be reconstructed.

The proposed novel method can thus bring insight into a range of applications, such as prediction of overpressure conditions in the subsurface, fracturing processes, degassing upon pressure drop.

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Combined Lu-Hf and Sm-Nd garnet-geochronology of lower crustal rocks from Val Strona, Ivrea Zone, Italy

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The Ivrea Zone (IZ, N-Italy) is a key locality to study metamorphic processes in the lower and middle continental crust. The Val Strona section of the IZ is particularly suited to study the timing of metamorphic processes along an increasing temperature gradient, comprising a continuous assemblage of granulite to amphibolite facies rocks. Therefore, three metapelites and one metabasite from the Val Strona section were examined in a combined Lu-Hf and Sm-Nd study, covering both amphibolite-facies and granulite-facies conditions. The samples were also investigated in terms of their petrology and geochemistry, in order to reconstruct the P-T-t path of the IZ rocks. In particular, representative garnets were investigated via electron microprobe (EMP) and LA-ICP-MS, determining their distribution patterns of major and some trace elements (REE, HFSE).

The EMP and LA-ICP-MS profiles in all investigated garnets lack any prograde zonation for 2+ elements (e.g. Mn) and Sm-Nd, whereas for Lu-Hf some growth patterns are preserved. The Lu-Hf ages obtained for the amphibolite-facies metapelites therefore presumably reflect garnet growth (278 ± 3 Ma; MSWD 2.3 and 279 ± 0.9 Ma; MSWD: 0.31). In contrast, the younger Lu-Hf ages obtained for the granulite-facies metapelite (263 ± 0.5 Ma; MSWD 0.9) and for the metabasite (249.6 ± 1.3 Ma; MSWD 2.0) are interpreted to represent cooling ages and document later cooling of the deeper crustal section. All Sm-Nd ages obtained in our study are about 30 Myrs younger than the respective Lu-Hf ages. Hence, the Sm-Nd ages likely represent cooling ages and may indicate retrograde diffusion-controlled re-equilibration processes. In conclusion, the results of this study point to a polyphase metamorphic evolution of the Val Strona section.
Correlation between crystallization patterns and diurnal growth bands in Scleractinian corals

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Diurnal growth bands are characteristic features of many scleractinian corals [1, 2] and are thought to be linked to the microstructure of the usually aragonite based mineral forming the coral skeleton. To shed light on this correlation we employed focused ion beam to create large (10 x 30 µm) thin lamellae for transmission electron microscopy enabling the detailed study of crystal morphology and orientation in spherulites of *Porites lobata*.

Figure 1: A) Randomly oriented nanocrystals with high porosity. B) Partly oriented nanocrystals with high porosity. C) Large acicular crystals orientated along the [0 0 1] direction (using the Pmcn spacegroup notation).

The investigations show a remarkable sequence of crystal morphology of randomly oriented, partly aligned nanocrystals and acicular crystals (fig 1). Selected area diffraction data shows that the morphology of the partly aligned nanocrystals is polycrystalline at the micrometer scale and no evidence for a non-classical growth mechanism (e.g. self assembly of small units; mesocrystal growth [3]) was found. The overall microstructural sequence is correlated with the observed optical contrast bands associated with a diurnal growth cycle. This is supported by TEM analysis of nanocrystal growth within aragonite needle-like bundles precipitated, using CaCO3 solutions with organics additives.


Experimental Investigation into the Density, Compressibility, and Phase Equilibria of the Northern Volcanic Plains on Mercury

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Knowledge of the density, compressibility, and other physical properties of magmas at high pressure is required in order to understand the differentiation of planetary interiors and secondary crust formation. With the recent estimates of Mercury’s surface composition from the X-ray spectrometer and Gamma ray spectrometer onboard the Mercury Surface, Space Environment, GEOchemistry and Ranging (MESSENGER) spacecraft, we now have our first opportunity to investigate the physical properties of magmas from the planet Mercury [1-3].

The Northern Volcanic Plains on Mercury (NVP) represent, to our knowledge, the most likely example of magmatic liquids that can be compositionally assessed from orbit with relatively high spatial resolution [1-2]. Although these NVP lavas may not represent primary, unfractonated partial melts of the mercurian mantle, they represent our best candidate to experimentally study magmas from the mercurian interior. Our goal is to determine the density and compressibility for a NVP composition using sink/float experiments in order to assess its eruptability onto the surface of Mercury.

We report the sinking of Fo100 spheres at 2.5 GPa, 3.5 GPa, and 5 GPa and temperatures of 1973 K, 2048 K, and 2223 K, respectively. We also report the floating of Fo100 spheres at 6 Gpa and 2323 K. With these results we can place tight constraints on the compressibility of this melt at 0.08 g/cm3/GPa. This is slightly more compressible than a komatiite (0.075 g/cm3/GPa) or peridotite (0.065 g/cm 3/Gpa) melt. Phase equilibria experiments are currently underway to determine a possible depth of origin for this melt. However, given its current density curve, the NVP composition is able to erupt at all pressures relevant to Mercury’s mantle as a result of buoyancy alone.

Triple oxygen isotope composition of photosynthetic oxygen and dissolved oxygen at saturation

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The measurement of biological production rates is essential for our understanding how marine ecosystems are sustained and how much CO₂ is taken up through aquatic photosynthesis. Traditional techniques to measure marine production are laborious and subject to systematic errors. A new biogeochemical approach based on triple oxygen isotope measurements in dissolved oxygen (O₂) has been developed over the last few years, which allows the derivation of gross productivity integrated over the depth of the mixed layer and the time-scale of O₂ gas exchange [1]. This approach exploits the relative ¹⁷O/¹⁶O and ¹⁸O/¹⁶O isotope ratio differences of dissolved O₂ compared to atmospheric O₂ to work out the rate of biological production. Two parameters are key for this calculation: the isotopic composition of dissolved O₂ in equilibrium with air and the isotopic composition of photosynthetic oxygen. Recently, a controversy has emerged in the literature over these parameters [2] and one of the goals of this research is to provide additional data to resolve this controversy. In order to obtain more information on the isotopic signature of biological oxygen, laboratory experiments will be conducted to determine the isotopic composition of oxygen produced by different phytoplankton species. In addition, the isotopic composition of dissolved oxygen at saturation will be measured under different temperature and salinity conditions.


Constraints on the creation of a HIMU-like isotopic reservoir beneath New Zealand

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The New Zealand microcontinent (Zealandia) formed as the active eastern margin of Gondwana. Upon cessation of subduction at ~110 Ma, extension led to opening of the Tasman Sea at 82 Ma, preceded by the formation of metamorphic core complexes, the opening and filling of half-graben structures and the intrusion of mafic dikes (~88 to 68 Ma). Subsequently, Zealandia has been punctuated by volumetrically minor, intermittent yet widespread intraplate magmatism from ~100 Ma through to recent times. This magmatism has typical OIB-like trace element abundances and radiogenic isotope compositions that trend towards a HIMU (high time integrated U/Pb) end member mantle composition. Recent publications have argued that that the intraplate OIB-like magmatism is not related to a mantle plume but is rather formed by delamination of mantle lithosphere, replacement by asthenosphere and associated partial melting. The variably diluted HIMU signature is interpreted to be the result of mixing between depleted mantle bearing a HIMU component with an Enriched Mantle or continental crust component.

New geochemical and isotopic analyses suggest the dike swarms also have an OIB-like chemistry. Initial Pb isotopic compositions of the dikes however are more similar to Pacific MORB. It is possible that the HIMU-like component in Zealandia is a result of trace element enrichment (with high U/Pb and Th/Pb) of a depleted mantle melt region in the Cretaceous. This source has remained stable beneath Zealandia while Pb ingrowth proceeded rapidly in U-Th rich domains. Repeated melt extraction from this source resulted in the intraplate magmatism with HIMU-like Pb isotopes. Isotopic data from peridotite xenoliths in the Cenozoic intraplate volcanoes reveal that the spinel facies lithospheric mantle beneath Zealandia also has high ²⁰⁶Pb/²⁰⁴Pb ratios. Lithospheric peridotite mantle is a potential source component for the intraplate basalts, which require an additional garnet rich source component.

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**Biomass burning as a major source of aerosols**

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It has been known for decades that biomass burning is a major source of aerosols, but recent advancement in satellite fire detection and biogeochemical modeling enables us better to quantify fire aerosol emissions and resulting concentrations. Here we show recent emissions estimates based on the new version 4 of the Global Fire Emissions Database version (GFED4) modeling framework and explain how climate and humans have shaped spatial and interannual variability in emissions over the past 15 years. We specifically highlight the role of fires not detected by the burned area algorithms but which can be seen in active fire data and occur often close to areas with relatively high population densities. We then focus on Indonesia which has the highest fire emissions density close to populated areas and show the relative importance of secondary aerosol formation on regional air quality.

**Assimilation of hydrothermally altered crust at slow spreading ridges**

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The process of crustal assimilation at mid-ocean ridges is not always obvious as assimilant and assimilator have similar bulk compositions. Hydrothermal alteration of oceanic crust significantly increases its chlorine (Cl) content, making Cl a potentially sensitive assimilation tracer. Although at fast spreading ridges this process has previously been shown [e.g. 1, 2], the intrinsically lower, more constant Cl values (~50-200 ppm) in basalts from slow spreading ridges make the tracing of crustal assimilation more arduous there.

We performed high precision Cl measurements in basalts from 3 slowly spreading ridges: the Southern Mid Atlantic Ridge (SMAR) at 7-10 °S (~3 cm/yr), the Red Sea at 16.5-26.5 °N (max. 1.6 cm/yr) and the Gakkel Ridge at 6 °W - 85 °E (max. 1.5 cm/yr). Chlorine contents vary from 40 to 400, 700 and 1300 ppm respectively, suggesting assimilation is occurring. Generally our Cl contents are higher than for average slow spreading ridges, although the Cl concentrations are not always elevated relative to elements of similar mantle incompatibility (e.g. K, Nb).

In the Red Sea and partially in SMAR samples we see a clear relation between Cl/K (as indicator of assimilation) and the presence of hydrothermal vents sites or tectonic features associated to these. In contrast, the also hydrothermally active [3] Gakkel Ridge has much lower Cl/K values, suggesting that other factors besides hydrothermalism play a role in the visibility of assimilation. The Cl contents of trace-element-enriched magmas (higher primordial Cl) at Gakkel Ridge are less sensitive to assimilation. In contrast, highly saline ocean water, brine pools and the presence of evaporites in the Red Sea make assimilation signals stronger there. Other influencing factors are the spreading rate and the type of rifting, i.e. volcanic or tectonically dominated. Through comparison of ridges with similar spreading rates and tectonic setting, we can examine the factors influencing the susceptibility of Cl concentrations to assimilation of altered oceanic crust.


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Smart air quality policies for a better climate: a regional analysis

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Feedbacks of climate policies on air quality (co-benefits as well as trade-offs) are now being recognized and introduced in optimization schemes for air quality policy development. However, also air quality policies can have consequences for climate. Some pollutants are contributing to warming (black carbon (BC), O3), others are cooling (SO4, NO3, organic carbon). Air quality policies are commonly designed without taking into account possible feedbacks on climate, although there is a potential for smart air quality policies that lead to a win-win situation for both climate and air quality.

In this work we evaluate the local and regional benefits of a portfolio of 16 climate-friendly, region-specific air quality measures that were identified in the frame of a recent UNEP-WHO assessment [1] [2]. These measures go beyond the baseline of current legislation and provide a global potential for 0.5K temperature reduction in the coming decades. A first group of measures addresses the reduction of CH4 emissions (with associated benefits for reduced background ozone), a second group targets BC (with additional benefits for O3 for those sectors where NOx and NMVOC are co-emitted species). The portfolio of measures was designed in order to yield a maximal climate benefit worldwide, but the measures also generate clear local and regional air quality and crop production benefits which may help to incentivise the implementation. This local and regional aspect was not explored in the UNEP assessments.

In our analysis we apply a global source-receptor model with a relatively high regional resolution (global coverage with 56 regions) to each of the measures. As a result we provide a region-specific ranking of the most relevant measures in terms of local and regional benefits.


Chemical stabilization of soil thallium using Mn(III,IV) oxide birnessite (δ-MnO2)

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The effect of highly crystalline birnessite (δ-MnO2) on Tl retention and bioavailability in contaminated soils was investigated. The stabilization/immobilization efficiency of the Mn oxide was evaluated on basis of Tl uptake by white mustard (Sinapis alba L.), sequential extraction and sorption experiments.

The obtained data clearly demonstrate that the application of birnessite to Tl-rich soils can effectively transform Tl from the labile (easily mobilizable) fraction to its reducible form, thus lowering Tl bioavailability and subsequent accumulation by plants. Substantial reduction of biological uptake of Tl was identified after the oxide application; the Tl levels in mustard tissues decreased by up to 50%, compared to the control treatment (non-amended soil).

The use of birnessite like soil additive might be an efficient and environment-friendly solution for soil systems contaminated with Tl. Nevertheless, further research focused on the long-term stability of the oxide in soil linked with Mn mobilization and potential toxicity for soil microbiota is needed before any general conclusion will be made.
Study of archaeological glass based on elemental imaging by laser ablation ICP-MS


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The study of ancient glass is predominantly focused on retrieval of its chemical composition to trace the provenance of raw materials, to unravel fabrication technologies and to investigate degradation phenomena. Techniques such as laser ablation ICP-MS are frequently used for multi-elemental microanalysis of glass in spot or raster mode. This work focuses specifically on the development of laser ablation ICP-MS techniques for lateral (2D) and volume (3D) imaging of glass to enhance the information retrieval. Spatial distribution analysis offers superior insight into the colocalization of elements to elaborate and advance archaeological hypotheses.

Fig. 1: 3D laser ablation ICP-MS protocol illustrated for imaging of Mg in a corrosion pit of an ancient glass artefact.

Laser ablation ICP-MS imaging techniques will be presented for 2D imaging based on rastering and quantification of the elements in the map using a so-called sum normalization technique which corrects automatically for drift and defocusing issues. Recently an innovative 3D imaging procedure was introduced based on laser drilling on a virtual grid on the surface using a burst of 50 laser pulses on each point of the grid (Fig. 1). After integration of the elemental peak areas, stacks of 50 2D depth maps with a depth resolution of 150 nm were retrieved which could be visualized as volume images. The application of the latter laser ablation ICP-MS imaging procedure will be demonstrated for the study of glass weathering mechanisms involved in the corrosion of some ancient glass artefacts.

Structure of Fe(III) precipitates formed by Fe(0) electrolysis in the presence of groundwater ions

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Oxyanions and bivalent cations influence the polymerization and precipitation of Fe(III) (oxyhydr)oxides, thus modifying the mineral structure in terms of local coordination environment of Fe, mineral phase, crystallinity, and oxyanion uptake mechanism. Few studies have investigated the interdependent effects of these ions on the formation of Fe(III) precipitates generated from Fe(II) oxidation, despite the co-occurrence of oxyanions and bivalent cations in natural waters. Such studies are essential to understand oxyanion mobility at both natural and engineered redox boundaries.

We combine wet chemical measurements and complementary synchrotron-based X-ray techniques (high energy X-ray scattering and Fe, As, and Ca K-edge X-ray absorption fine structure (EXAFS) spectroscopy) to investigate the interaction between oxyanions (PO43-, AsO43-, SiO44-) and bivalent cations (Ca2+, Mg2+) and their subsequent effect on the formation of Fe(III) precipitates. Fe(III) precipitates were produced by the electrolytic dissolution of an Fe(0) electrode in an electrolyte consisting of oxyanion concentrations ranging from 0.05-0.5 mM and the presence or absence of 1 mM Ca2+ or Mg2+.

Our results suggest a systematic decrease in the strength of bivalent cation:oxyanion interaction in the order of Ca>Mg>P>As(V)>>Si. We find that 1 mM Ca2+ enhances the uptake of As(V) (per mass of Fe) more than 1 mM Mg2+. Whereas Fe(0) electrolysis leads to 2-line ferrihydrite-like material in the presence of 0.05 mM As(V) alone (initial As/Fe = 0.1), the presence of 1mM Ca2+ with 0.05 mM As(V) promotes the formation of more crystalline lepidocrocite-like material. These results are consistent with a strong Ca-As(V) interaction that can modify the extent of As(V) uptake and the resulting Fe(III) precipitate structure. Ca K-edge XAS data in the Ca:As concentration series display features consistent with second-shell As(V) scattering. No discreet As(V)-Ca surface-precipitate is observed. Our results indicate that direct Ca-As(V) interactions must be considered when assessing iron and arsenic biogeochemistry.
Use of LA-ICP-MS and MC-ICP-MS in a biomedical context

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Solution nebulization ICP-MS was exploited since its commercial introduction in the 1980s for the analysis of body fluids. Also elemental speciation using a combination of a chromatographic or electrophoretic separation technique and ICP-MS as a very sensitive and element-specific detector was rapidly deployed in a biomedical context. However, for a long while, both direct analysis of solid materials using laser ablation LA-ICP-MS and isotopic analysis of metallic and metalloid elements using MC-ICP-MS largely remained the domain of geochemical applications. More recently however, also the capabilities of these approaches in a biomedical context are being discovered as will be illustrated in this presentation using applications from the UGent lab.

As a result of the laser beam dimensions (typically from < 5 to > 100 µm diameter) and the sub-µm penetration depth per shot, LA-ICP-MS is also suited for spatially resolved analysis of thin sections of entire small animals and/or selected body parts. By scanning such a section line per line, the distribution of a target element can be visualized in a map. It will be shown how this approach can be used for documenting the distribution of a Br-containing anti-tuberculosis drug across the body compartments of rat or the penetration of a Pt-containing chemotherapeutic drug in cancer tissue after intraperitoneal treatment.

MC-ICP-MS was relied on for isotopic analysis of the essential transition metals Fe, Cu and Zn in human whole blood and/or serum. The isotope ratio results obtained for a reference population were evaluated with the aim of revealing the influence of factors such as gender and feeding habits. A link between the Fe isotope ratio results and the parameters used to describe Fe status (among other, ferritin and transferrin levels) was established. Isotope ratio results obtained for blood from patient groups (e.g., hemochromatosis, anemia of chronic disease ACD, Wilson’s disease) were compared to those of the reference population with the aim of investigating the potential of isotopic analysis as a diagnostic tool, capable of revealing diseases that otherwise can only be diagnosed at a later stage or via more invasive methods.

Novel particle method for modelling melt generated heterogeneity in spherical mantle convection models

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Today there are extensive geochemical databases of surface observations but they lack satisfying geodynamical explanations. Working towards this goal we implement a new way to track chemistry in the well developed mantle convection code TERRA.

The bulk composition and trace element abundance (all isotope of He, Ar, U, Th, Pb, K) are tracked via particles. One value on each particle represents bulk composition, which represents the basalt component. Chemical alteration of bulk composition and trace elements happens at self-consistent, evolving, melting zones. We use a composition dependent solidus, therefore the amount of melt generated depends on pressure, temperature and bulk composition. A novel aspect is that we do not move particles that undergo melting; instead the chemical information carried by a particle is transferred to other particles. Melt is instantaneously transported to the surface, thereby increasing the basalt component carried by the near surface particles and decreasing the basalt component in the residue. As melt arrives at the surface, a fraction of its content of trace elements is moved into separate continent/atmosphere reservoirs. For trace elements in the continent, delayed return to the top of the mantle, simulates erosion and recycling back into the mantle.

Results of our implementation will show the evolution of: 1: bulk composition. 2: melt amount. 3: concentration and abundance of trace elements in the atmosphere, continent, melt and surface layer.

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The impact of element speciation on apparent partition coefficients

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Liquids, including aqueous fluids and silicate melts, are strongly underrepresented in the geologic record. This is unfortunate, because fluids and melts play a disproportionately large role in the mobility and cycling of elements, as well as in the rheology of the Earth. To constrain the compositions of these liquids we commonly turn to cogenetic minerals, which are readily available in the geological record, and reconstruct liquid compositions using data on the partitioning of elements among minerals and fluids. Lattice-Strain Theory (LST) provides the reference frame for understanding the systematics of this partitioning, by linking partition coefficients to the extent of charge and/or radius mismatch of an element in the mineral lattice [1]. A large mismatch results in a low partition coefficient and vice versa. This partitioning approach has proven highly successful for silicate melts, and is equally applicable to mineral-aqueous fluid systems [2]. However, partitioning studies are generally mineral-centric and regard the liquid as a passive reservoir from which the mineral selectively incorporates elements depending on their fit. It thereby ignores the variable complexation, or speciation, of elements in melts and fluids.

We have evaluated the impact of speciation on partition coefficients by experimentally determining the trace element partitioning behaviour among minerals and fluids in aqueous solutions with varying ligands. Experimental results, complemented with data from natural systems, show that differences in speciation among the elements change apparent (i.e. measured) partition coefficients by up to 4 orders of magnitude. Speciation exerts control on partitioning by determining the concentrations of the species involved in element uptake [2]. If speciation is known, this effect can be incorporated in LST modelling by correcting concentrations for the proportion of an element present in the species relevant to element uptake.

We conclude that the liquid is not a passive reservoir in element partitioning with minerals. Speciation effects have to be accounted for to accurately reconstruct liquid compositions from minerals. However, if speciation is known, its effects can readily be accommodated in Lattice-Strain Theory.


Aluminium in an ocean general circulation model and observations

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The distribution of dissolved aluminium (Al) in the ocean is of interest because of the impact of Al on remineralisation of diatom opal and the use of surface ocean Al as a tracer for dust. The main thermocline Al concentration has been simulated reasonably well with only a dust source and scavenging as the removal process [1].

In this study the simulation is significantly improved by the addition of a sediment resuspension source (Fig. 1). This supports the idea that the most significant sources of Al to the ocean are dust deposition and sediment resuspension.

Figure 1: Modelled dissolved aluminium concentration at four depths in the world ocean. Observations as coloured dots. Both simulated and observed concentrations are in nM. Experiments with biological incorporation have been performed as well. These show that this can be an important removal process.

Fluid-rock interaction along plate boundary shear zones: insights from modern and ancient examples

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Field observations and geophysical investigations on modern and ancient plate boundaries reveal that these shear zones are several 100’s to 1000’s m thick. Marine geophysicists usually see this zone as a low p-wave velocity horizon that implies high fluid content. Onland, ancient plate boundaries are characterized by evidence for incorporation of unlithified, fluid-rich sediments into the fault zone. A better idealization of this dynamic system should consider rock/sediment and fluid supply to the channel, the heterogeneity of deformation, and the evolution of PT conditions as the deeper parts of the shear zones are reached. The upper and lower boundaries of this system can migrate towards the upper or lower plate, defining the main tectonic processes shaping the margin, but also influencing the processes that are responsible for earthquake nucleation, rupture and propagation. Within the shallow, <15 km deep part of the plate boundary shear zone, a gradual change of physical properties defines three subregions; zone 1 of rapid fluid dewatering, zone 2 of overpressure, and zone 3 with metamorphic fluid release. These implications are that a subduction shear zone is a dynamic feature with along-strike and down-dip variations caused by changes in channel material, in trapped fluids, and in interplate boundary geometry.

Release of solid-bound phosphate during the sulfidization of lepidocrocite

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Natural ferric iron (oxyhydr)oxides often carry oxyanions such as phosphate or arsenate either adsorbed onto their surfaces or incorporated inside their structure. As a consequence, reductive dissolution of iron (oxyhydr)oxides can lead to the release of the initially solid-bound oxyanions. This link between iron reduction and the mobility and bioavailability of oxyanions is widely recognized but little is known about the kinetic coupling of oxyanion mobilization and iron reduction as well as the underlying mechanisms. Here, we investigated the release of phosphate from lepidocrocite (γ-FeOOH) during its reaction with dissolved sulfide in flow-through reactor experiments at pH values around 7.5 and 8.5. Two types of lepidocrocite were used: One containing structurally bound phosphate, and a second with only adsorbed phosphate. The release of structurally bound phosphate followed the progress of sulfidization and the rates of sulfide consumption were linearly related to the rate of phosphate release. In general, the reaction with sulfide proceeded faster at pH 7.5 than at pH 8.5 and, in turn, phosphate was mobilized faster at pH 7.5. In experiments with adsorbed phosphate, addition of sulfide to the inflow solution led to a pronounced phosphate pulse in the outflow. This quick release can be attributed to ligand exchange reactions in which dissolved sulfide replaces phosphate in surface complexes. However, not all of the adsorbed phosphate was instantaneously removed from the surface. The mobilization of the remaining adsorbed phosphate followed the progress of lepidocrocite sulfidization similar to the behavior of structurally bound phosphate. Furthermore, the fraction of instantaneously released phosphate was smaller at pH 7.5 than at pH 8.5. We propose, that these phenomena can be explained by the different reactivity of bidentate and monodentate phosphate complexes, whereas the latter are more abundant at pH 8.5. That is, phosphate in monodentate complexes readily undergoes ligand exchange with sulfide while bidentate phosphate complexes are relatively inert towards the attack by sulfide. Our results show that the pH effect on phosphate release in anoxic environments can be oppositional depending on the binding form of phosphate.
Formation of the IIE non magmatic iron meteorites

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The well preserved ~450 kg fragment of the IIE non-magmatic iron (NMI) Mont Dieu II (MDII) meteorite [1] has been investigated to understand the formation of IIE NMI meteorites that are not directly related to core formation [2]. The present study focuses on the abundant large silicate inclusions of MDII, studied under SEM/EDX, and for which major and trace elements were measured by ICP-OES & ICP-MS. Oxygen isotopes were measured by laser-fluorination.

The silicate inclusions are characterized by coarse-grained granular texture, crossed by metal veins. Round structures (~ 1 mm) composed of ferromagnesian minerals are present, interpreted as relict chondrules. Three well-preserved barred olivine chondrules, a feature so far only described for Netschaëvo NMI IIE [3], and glass have been observed. Low Ca-Px, Ol and albite Pl are the major mineral phases. FeO-rich glass (interpreted as relict from the impacted body), Chr, Tro, Schr, (chlor)Ap and Fe-Ni metal are found as minor phases. The δ17O of MDII is 0.714±0.024 ‰. The Fa and Fs molar contents of the relict chondrules are similar to those observed in H-type OC. The IIE NMI seem also related to OC based on their oxygen isotopic compositions [4], as the δ17O of MDII falls within the range defined for H 3-6 OC [4; 5].

Based on these results, an impact formation model is proposed, where a Fe-Ni impactor collided with an H-chondrite parent body. A position near the edge of the asteroid and at a shallow depth of the magma pool is favored for MDII, because fast cooling is necessary to preserve the chondrules and glass. After this first stage of fast cooling, a second phase involving slower cooling is needed to permit the development of the Windmanstätten pattern.


The composition of the lower crust of the Oman Ophiolite

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Fundamental questions remain as to where, how, and to what extent chemical fractionation occurs in the oceanic lower crust and upper mantle, prior to eruption of MORB. There is no continuous drill core through oceanic crust in situ. Thus, to address these questions, we turn to the Oman ophiolite, where there is a continuous section from residual mantle peridotite to submarine lavas formed at an oceanic spreading ridge.

We present a detailed, stratigraphically-constrained, bulk composition for the lower crust of the Wadi Khafifah section of the Oman ophiolite. Together with sheeted dikes and lavas having trace element contents similar to MORB, the bulk crustal composition meets two fundamental criteria for a mantle-derived melt: (1) It has Mg# in equilibrium with Fo90 mantle olivine; (2) it is multiply saturated in ol+aug+plag/sp at shallow mantle pressures. In addition, clinopyroxene crystallizes early, eliminating the so-called ‘pyroxene paradox’. The parent magma – with major element composition indistinguishable from primitive MORB – represents an aggregate produced by polybaric decompression melting of depleted MORB mantle (DMM), which has crystallized approximately 5% olivine – probably by reactive fractionation (Collier & Kelemen, J Petrol 2010) in the crust-mantle transition zone – prior to emplacement within the crust. An additional 40-60% fractional crystallization (ol+aug+plag) in the lower crust is required to produce the observed sheeted dike and lava compositions. Where data are available for comparison, gabbro compositions reported here are similar to analysed samples from modern fast-spreading mid-ocean ridges. Thus, our results are relevant for understanding modern fast-spreading oceanic crust.
Uranyl on Mg-rich minerals: Polarisation Dependent EXAFS

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In the UK, large quantities of intermediate level waste pose complex radiological remediation challenges. Chemical understanding of uranium in these Mg-rich sludges is vital. By applying two EXAFS techniques, we determined: (1) where uranyl (UO22+) is adsorbed, and (2) how uranyl attaches to the mineral surface. Powder experiments with U(VI) were performed with magnesite [MgCO3], brucite [Mg(OH)2], nesquehonite [MgCO3·3H2O] and hydromagnesite [Mg5(CO3)4(OH)2·4H2O] Kd values for the Mg-carbonate powders were comparable to or exceeded published results for Ca-carbonates. A second set of experiments (GIXAFS) used single crystals of magnesite (10.4) and brucite (0001). Single crystals were reacted under ambient and reduced PCO2 ~ -4.5 for 48 hrs. with concentrations of U(VI)-chloride above and below the solubility of schoepite [UO2(OH)2·H2O] (ca. 40% U(VI) adsorbed). GIXAFS measurements were made at \( \chi = 0^\circ \) and \( \chi = 90^\circ \) relative to the synchrotron beam polarisation. GIXAFS results clearly showed polarisation dependence for both ambient and reduced PCO2. XANES results showed uranyl is oriented with the axial oxygens perpendicular to the mineral surface. The EXAFS structural model corroborates an uranyl-tris carbonate. This implies local rutherfordite-like [UO2(CO3)3] regions which may polymerise at high uranyl activities into a thin film. These results are useful for predicting uranium behaviour during disposal and remediation. The development of in-situ measurements is currently in progress.

Mass-independent sulfur isotope signature in spherule beds of the 3.4-3.2 Ga Barberton Greenstone Belt, South Africa

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Theoretical and experimental studies have shown that atmospheric SO2 isotopologue self-shielding effects in the 190-220 nm region of the solar spectrum are the likely cause for mass independent fractionation of sulfur isotopes (S-MIF). The main products of this photochemical reaction – SO3 and S0 – typically define a compositional array of ca. \( \delta^{34}S = 0.6 \) \( \delta^{34}S \). This is at odds with the generally observed trend in Archean sulfides, which broadly defines an array of \( \delta^{34}S = 1.4 \) \( \delta^{34}S \). Various explanations have been proposed, including a diminution of \( \delta^{34}S \) caused by chemical and biogenic mass-dependent fractionation of sulfur isotopes (S-MDF), mixing with photolytic products produced during felsic volcanic events, or partial blocking of the low-wavelength part of the spectrum due to the presence of reduced atmospheric gases or an organic haze.

Early in Earth’s history large meteorite impacts would have ejected dust and gas clouds into the atmosphere that shielded solar radiation and affected global climate. It is thus likely that at certain time intervals of high meteorite flux the atmosphere was significantly perturbed, possibly leaving anomalous sulfur isotopic signatures in the rock record. Here we describe the sulfur-MIF and -MDF signatures in sulfides of spherule beds S2, S3 and S4 of the Barberton Greenstone Belt, South Africa. In particular in spherule bed S3 – and to a lesser extent S4 – a trend of \( \delta^{33}S/\delta^{34}S = 0.7 \) is observed that closely follows the expected trend for SO2-photolysis in the 190-220 nm spectral range. This suggests that an impact dust cloud (deposited as spherule beds), which sampled the higher region of the atmosphere, specifically incorporated products of SO2 photolysis in the 190-220 nm spectral range. This trend indeed appears to be the result of additional photochemical reactions that took place in the lower part of the atmosphere.
Geochronology of Weathering and Pedogenesis

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The combination of \textsuperscript{40}Ar/\textsuperscript{39}Ar, (U-Th)/He, and U-series dating of weathering-product and pedogenic Mn and/or Fe oxyhydroxides permits determining the chronology and rate of chemical reactions in the weathering crust. These methodologies are complementary and suitable for dating processes spanning from Recent to the earliest preserved weathering profiles on Earth. The application of these methods in weathering geochronology reveals that minerals hosted in pedoliths are invariably much younger than minerals preserved in the underlying saproliths, indicating that the pedolith has a much greater propensity to undergo mineral dissolution-reprecipitation than the remainder of the weathering profile. The greater reactivity of the pedolith appears to be controlled by organic activity, mechanical and chemical, which promotes frequent and recurrent mineral dissolution-reprecipitation. In contrast, the underlying saprolith appears to record the influx of weathering solutions during the early stages of evolution of a weathering profile. Once precipitated, saprolith minerals may remain in metastable equilibrium, sometimes for millions or tens-of-millions of years. Saprolith minerals become more prone to dissolve and reprecipitate when the pedolith front advances into the saprolith, but only during drastic changes in weathering conditions do minerals within the saprolith undergo dissolution-reprecipitation. Identifying and dating the multiple generations of supergene minerals in both the pedolith and saprolith reveal a history of weathering that is protracted and episodic, particularly in the case of deep and stratified lateritic weathering profiles. The major challenges in applying these geochronological approaches to the study of weathering and pedogenesis is the difficulty in identifying and physically sampling distinct generations of supergene minerals. This challenge is particularly acute in the pedolith.

Gas discharges for continental Spain: Geochemical and isotopic features

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In this work the results of a geochemical and isotopic survey of 37 gas discharges was carried out in continental Spain are presented and discussed. On the basis of the gas chemical composition, four different areas can be distinguished, as follows: 1) Selva-Emborda (SE) region; 2) Guadalentin Valley (GV); 3) Campo de Calatrava (CC) and 3) the inner part of Spain (IS).

The SE, GV and CC areas are characterized by CO\textsubscript{2}-rich gases, while IS has N\textsubscript{2} as main gas compound. The CO\textsubscript{2}-rich gases can be distinguished at their turn on the basis on the helium and carbon isotopic composition. The SE and CC areas have a strong mantle signature (up to 3 Ra). Nevertheless, the carbon isotopic composition of CC is within the mantle range and that of SE is slightly more negative (down to -8‰ PDB). The GV gases have a lower mantle signature (6 Ra) with respect to SE and CC and more negative carbon isotopes (10‰ PDB). It is worth to mention that the SE, GV and CC areas are related to the youngest volcanic activity in continental Spain, for example the Garrotxa Volcanic Field in Catalonia records the latest event dated at 10,000 years, and the isotopic features, particularly those of helium, are suggesting the presence of magmatic bodies still cooling at depth. The N\textsubscript{2}-rich gases, i.e. those from the IS area, has an atmospheric origin, as highlighted by the N\textsubscript{2}/Ar ratio that ranges between those of air and ASW (Air Saturated Water). The isotopic composition of carbon is distinctly negative (down to -21‰ PDB) and that of helium is typically crustal (0.02-0.08 Ra), confirming that these gas discharges are related to a relatively shallow source.

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The microstructural study of clay minerals - polymer matrix nanocomposites.

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Clay minerals (layered silicates) have been used as reinforcing filler for polymers. Montmorillonite (MMT) has well-known 2:1 layered structure where the central octahedral alumina sheet is sandwiched by two tetrahedral silicate sheets with cations such as Na+ or Ca2+, which are present between layers to compensate the net negative charge. The lateral dimensions of MMT particles vary from tens to hundreds of nm. The interlayer cations can be replaced by organic molecules through a intercalation and further exfoliation. Two processes were crucially important: the ability of MMT particles to intercalation and exfoliation and the dispersion of the clay particles in the polymer matrix. The MMT particles, organomodified particles and 1, 3, 5, 7 wt% MMT filled polymer (polyimide) were studied by transmission electron microscopy and microanalysis. The interplanar distance in the MMT particles determined from the number of high resolution images and electron diffraction pattern was found to be of \( c = 0.99 \pm 0.01 \) nm. The edge type dislocation with projection of burgers vector \( b = c [001] \) were observed. The interplanar distance \( c \) in the organomodified particles mostly increase to 2.2 – 2.5 nm together with the growth of dislocation density. The study of MMT-polymer nanocomposites demonstrated the enhancement of particles dispersion in the range of 1 to 5 wt% filled polymer with the growth of the exfoliated particles density. Much less exfoliation of the MMT particles were found in 30 wt% filled composite together with formation of high density of pores, observed in these TEM specimens.

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Phase relations of carbonate eclogite during subduction and the effect of redox conditions on diamond – carbonate reactions

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High pressure experiments are critical to understanding the recycling of carbon into the deep earth during subduction processes [1,2]. Melting and phase relations of carbonate eclogites (former altered oceanic crust) and the effect of oxygen fugacity on diamond versus carbonate stability along deep subduction geotherms are currently very poorly understood.

To investigate this, a series of piston-cylinder experiments was conducted at \( P = 3.5-6.0 \) GPa, and \( T = 900-1300^\circ C \). Starting material for the first part of the study models highly carbonated (10% CaCO3) altered oceanic basalt [1]. Experiments at reduced conditions (using Fe capsules) showed the absence of crystalline carbonate and the presence of siliceous near-solidus melts. In high oxygen fugacity experiments, performed using a Re-ReO2 buffer at 1000-1100°C, carbon was present as carbonates at high pressure (5.5GPa) and in carbonate-silicate melt at low pressure (3.5 GPa).

The stability of carbon versus carbonate in subducting C-bearing eclogite may be defined by reaction \( \text{CaMg(CO}_3\text{)}_2 + 2\text{SiO}_2 = \text{CaMgSi}_2\text{O}_6 + 2\text{C} + 2\text{O}_2 \) [3]. This reaction is being investigated in a second series of experiments with compositionally variable carbonate eclogites (mixes of synthetic garnet, clinopyroxene, kyanite, coesite, dolomite and Ir metal as a redox sensor) being used to determine \( P-T-f\text{O}_2-X \) phase relations. Garnet Fe3+ contents will be determined using the electron microprobe based flank method [4] and the synchrotron based Fe K-edge XANES method [5].

Petrology of the lamprophyres.

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Chuya complex of mica lamprophyres situated in the southeast part of Gornyi Altai and extends to Mongolia. Dikes of this complex are distributed irregularly and form the belts or the areas accompanying fault zones. Lamprophyres from two largest areas, named south-chuya and yustyd respectively, were characterized in geological, petro- and geochemistry terms. Radiological characteristics give evidence of synchronic formation of the dikes from different areas. Bulk-rock analysis indicates, that the rocks are basic to intermediate, calc-alkaline and ultrapotassic. On the most petrochemical and geochemical binary plots the rocks of dykes from different areas fully or partially overlap. The multi-element and rare-earth diagrams of all investigated rocks are equal in the form, at the position of HFSE minima, have high La/Yb (17-62) and Gd/Yb (4-9.7) relations. Geochemistry characteristics allow us to suggest that all rocks were formed as a result of small degrees partial melting of garnet mantle source. However, in our studies, fundamental differences in the isotopic composition of Nd and Sr and some petrochemical features have been established. For the yustyd area rocks the initial isotopic relations are closes to BSE. And for the lamprophyres from another area Nd varies from (-2.84 - - 4.05) and 87Sr/86Sr>0.70858. In our work we discuss three hypotheses forming the lateral variability in composition of the lamprophyres of the Chuya complex: 1) heterogeneity of the mantle; 2) contamination the rock forming melt by crust material; 3) liquid immiscibility, accompanied by redistribution of some major and trace elements.

The role of fluoride-silicate liquid immiscibility in REE ore genesis

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The Mid-Proterozoic peralkaline Strange Lake pluton (Québec-Labrador, Canada) hosts potentially economic concentrations of high field strength elements (HFSE), including the rare earth elements (REE), zirconium and niobium in zoned (Zr-rich borders and Ca-F-REE-rich cores) and unzoned pegmatites. Based on bulk rock geochemistry, mineralogy and fluid inclusion data, HFSE enrichment in the pluton has previously been interpreted to be due to extreme fractional crystallization and late hydrothermal alteration. However, recently collected melt inclusion data suggest that a third process, namely melt immiscibility, may have played an important role in the concentration of the HFSE.

Three types of melt inclusion have been identified in quartz from the Strange Lake granite after heating to 900-950 °C and quenching. Type 1 inclusions are composed of silicate glass and display enrichment in Zr, Nb and Ti with increasing alkalinity. Type 2 inclusions also contain silicate glass and, in addition, a globule of a REE-bearing calcium fluoride glass (up to 14 wt. % REE). Type 3 inclusions contain calcium fluoride glass with multiple silicate globules. Calcium fluoride glass in both Type 2 and 3 inclusions contain calcium fluoride glass globules. Calcium fluoride glass in both Type 2 and 3 inclusions contains a REE fluoride melt. We propose that fractional crystallization enriched the magma in fluorine, leading to silicate-fluoride liquid immiscibility prior to and during emplacement of the pegmatites. This caused partitioning of Zr, Nb and Ti into the silicate melt and F, Ca and REE into the fluoride melt. Further evolution of the melts occurred separately. Quartz, feldspars and arfvedsonite crystallized from the silicate melt, enriching the latter in Zr, Nb and Ti, and fluoride crystallized from the fluoride melt, enriching its residue in REE. The latter melt eventually exsolved a REE-fluoride melt.

The observed zoning of many pegmatites is interpreted to reflect crystallization of the silicate melt, including formation of zirconosilicates in the outer zone, and migration of exsolving or heterogeneously incorporated (prior exsolution) calcium fluoride melt inwards. This latter melt subsequently exsolved a REE-fluoride melt and the two melts crystallized to form the fluorite- and REE mineral-rich pegmatite cores. To our knowledge, this study provides the first example, in which silicate-fluoride liquid immiscibility has been shown to help concentrate the REE to potentially economic levels.
Volatilization of Hg from HgS minerals mediated by the coupled activity of thiosulfate and a sulfur-oxidizing bacterium


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Soils and sediments, where mercury (Hg) can exist as the Hg sulfide mineral metacinnabar (β-HgS), represent major Hg reservoirs in aquatic environments. Due to its low solubility, metacinnabar has historically been considered an insignificant source of Hg to the aqueous environment. Our previous work has shown that bacterial colonization of metacinnabar incubated in the shallow sediments of the Hg-contaminated East Fork Poplar Creek (Oak Ridge, TN) is dominated by genera known to use reduced sulfur compounds as electron donors during growth. Based on 16S rRNA pyrosequencing, Thiobacillus thioparus, an obligate autotrophic neutrophilic sulfur oxidizer, is among the most abundant colonizers.

Here we show that T. thioparus incubated aerobically in the presence of metacinnabar and thiosulfate (0.1-20 mM) results in substantial metacinnabar dissolution and release of Hg. Upon reaction, sulfate concentrations are higher than can be attributed to oxidation of thiosulfate alone, yet aqueous Hg(II) concentrations remain below detection limit. We show that in the presence of metal cultures of T. thioparus aqueous Hg(II) released following HgS dissolution is rapidly volatilized forming Hg(0). In control incubations (media with thiosulfate and metacinnabar, and no viable cells) thiosulfate volatilized forming Hg(0). In control incubations (media with thiosulfate) Hg(II) released following HgS dissolution is rapidly volatilized forming Hg(0) suggesting that thiosulfate, a strong Hg-binding ligand, abiotically induces HgS dissolution. T. thioparus possesses genes involved in the Mer detoxification pathway, and we are currently investigating mer expression in this system.

These findings have important implications for environmental Hg cycling, highlighting the unappreciated potential of Hg release from assumed permanent solid-phase Hg sinks. It further introduces new pathways for solid-phase Hg to enter the global atmospheric mercury pool.

Role of deep carbides in the formation of hydrocarbons?

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Whether hydrocarbons in rocks are inorganic or organic in origin might be evaluated by considering carbides as precursors in the formation of deep hydrocarbons and a range of volatile compounds, since carbide may constitute >2 wt% of the Earth’s core [1].

Low pressure carbides can be (a) Interstitial (Ti, V, Cr, Zr, Nb, Hf, Ta, W) (b) Covalent (B, Si): (c) Intermediate (Ti, V, Cr, Mn, Fe, Co, Ni): or (d) Salt-like (Groups I, II, and III). In the absence of high-P experimental data, groups (a) (b) and (c) should be included as candidates for carbides found in the inner core, because they are stable at high-T: they also react with water and/or oxygen to form hydrocarbons and CO or CO2 respectively. Carbides can be described as ‘reactive minerals’ [2] and react with water to yield hydrocarbons. Hydrocarbon pathways from CH4 at high-P have started to be explored [3].

Siderophile element carbides (Cr, Fe, Ni, V, Mn, Co) hydrolise with water to yield “organic matter”[4]. We propose similar reactions based on carbides of Ca and Al for the formation of methane hydrate. The reactions are expected to be of the general type: MxCy +nH2O where M is the metal = Hydrocarbons such as CH4 +M(OH)2. In the presence of oxygen such hydrocarbons would react to form CO and ultimately CO2. Similar reactions could occur with nitrides, sulphones and silicides. These compounds are stable at high-T and would react with water and oxygen at lower temperatures.

Methane hydrates are common in continental shelf sediments and in deep arctic permafrost and occur at depths of around 500m [5]. Methane is found under lakes such as Lake Kivu [6]. It is generally assumed that such deposits are of biological origin. However, no explanation is given as to how complex molecules form organic deposits. Synthesis routes at high-T are well known, but we propose experiments to high-P conditions to test whether deep carbides [7] act as possible precursors in the abiogenic synthesis of hydrocarbons and methane hydrates.

Nano and Bulk-Scale Characterization of Biogeochemical Processes: A Case Study

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Recent advances in nanotechnology and analytic instrumentation allow biogeochemical processes between microbes, metals and minerals to be probed at remarkable levels of complexity, sensitivity, space and time. One of the dominant trends in geomicrobiology is the detailed characterization and application of biogenic minerals whose characteristic features are at the nanometer scale in at least one dimension. It is therefore important to understand – and ultimately exploit – the unique properties and behavior of a wide range of nanoscale biogenic materials. Central to this trend are the development and application of effective analytic techniques for characterizing the structural and chemical properties of biogenic minerals with (sub)nanometer spatial resolution.

Microbes in the subsurface are involved, directly or indirectly, in a plethora of activities such as metal reduction and oxidation, mineral precipitation and dissolution. These innate capacities of subsurface microbes are often exploited for in situ remediation of contaminated sites. During subsurface bioremediation of uranium-contaminated sites, indigenous metal and sulfate-reducing bacteria may produce biogenic minerals such as mackinawite (FeS) which could potentially drive abiotic uranium reduction.

In this work, the propensity of well-characterized biogenic mackinawite to abiotically reduce U(VI) was tested using a suite of electron microscopy and synchrotron based spectroscopy techniques. High-resolution electron microscopy confirmed the formation of nanoparticulate uraninite [UO2] on the surface of biogenic mackinawite, which was further confirmed with bulk X-ray absorption spectroscopy that revealed the molecular coordination environment of uraninite. X-ray photoelectron spectroscopy confirms that U(IV) reduction was coupled to the oxidation of S2- and not structural Fe(II) within the biogenic mackinawite. The combination of rigorous nano- and bulk-scale characterization provides insights into such biogeochemical processes, that occur during subsurface biostimulation, that are not always possible with bulk-scale analyses alone.

Unravelling complex groundwater recharge and transport of contaminants using combined stable and radioactive isotope tracers

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As part of a project assessing the quality and potential of groundwater, a vital resource in the extremely arid but touristic Namib-Naukluft area, a geochemical study of the surface and groundwaters, plants, soil, and rocks was undertaken. The study indicated excessive nitrate concentrations in about 15% of the 70 groundwaters sampled (several 100’s of mg/l). While many of these groundwaters with high NO3 also have high δ15N and δ18O values and are from boreholes close to settlements, others are not. Furthermore, the vegetation also has elevated δ15N values, making it difficult to identify anthropogenic or animal watses as contaminants. Mean residence times of groundwaters estimated by 14C measurements of DIC have a wide range (recent as >100% modern carbon to about 14’000 yrs b.p.), and also a wide range of δ13C values (–4.6 to –12.8‰) related to infiltration across soils of typical C3 (mountains) and C4 (savannah-desert) type of vegetation and limestone-derived soils and aquifers (δ18O of –3 to +2‰). This variation, in addition to drainage across calcrite soils during brief periods of recharge necessitates substantial corrections to the measured 14C ages, but which can be modelled via the concentrations and stable isotope compositions of DIC.

Recharge during decadal “extreme events” is suggested by the H- and O-isotope compositions of the groundwaters with low δ-values compared to normal average annual rainfall. Seasonal variations in H- and O- isotope compositions in combination with modern mean residence times and high high nitrate δ15N and δ18O values thus do confirm an anthropogenic/animal-waste origin. The complex recharge of the aquifers across different soils, soil organic matter, can hence be unravelled using a combined isotopic tracing approach. In general, a slow, horizontal flow away from the principal mountain-recharge area, but also with locally important vertical recharge, particularly close to settlements and man-made boreholes, is indicated.
Isotopically light (Solar?) nitrogen associated with the planetary noble gas carrier (Q)

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The nature of the planetary noble gas carrier (Q) has remained an intriguing cosmochemical puzzle for decades. Q can be significantly enriched by dissolving all meteoritic silicate minerals to leave behind only carbonaceous material and oxides. However, even after that, the abundance of Q in the residue is much less than 1%. This is the main reason why Q is so difficult to identify. Therefore, Q is characterised indirectly by its properties, such as its susceptibility to oxidation or its resistance to parent body metamorphism compared to macromolecular materials as well as by the noble gas components it contains. Such observations suggest that Q has been formed very early in the Solar System, or may even predate it formation.

Our analyses of a number of CR meteorites using our multi-element isotope analyser, Finesse, in combination with stepped combustion, has revealed a new property of Q – its separation from most of macromolecular carbon and nitrogen. In CR2 and CR3 petrological groups, but not in CR1s, the Q noble gases, are released in a narrow range at a high temperature (~1100 °C). It appears that Q somehow becomes isolated within the matrix from direct contact with oxygen gas during stepped combustion. Only when the matrix opens up does oxygen react with Q (oxidising it almost instantly). Since almost no macromolecular C and N remains by the time of Q oxidation, the Q nitrogen dominates the release at these temperatures. And, as such, its isotopic composition is revealed. The lowest measured δ¹⁵N associated with the noble gas release at the high temperatures is -140‰. And this is only the upper limit since a certain amounts of other (isotopically heavier) N components are also present along with Q nitrogen. We believe that Q nitrogen is likely to have δ¹⁵N similar to solar composition (-380‰) determined by the Genesis mission. The presence of solar N in Q is also consistent with its He isotopic composition corresponding to pre-deuterium burning era of the early Solar System.

On the importance of ternary alkaline earth carbonate complexes of uranium(VI) in natural waters: a round-robin modeling test

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The availability of uranium in natural waters is governed by many processes and interactions with chemical compounds. At equilibrium the predominant soluble and solid forms of uranium can be estimated using thermodynamic data and aqueous geochemical speciation codes. The quality of calculations is mainly related to the quality and completeness of the entry data. Within the working group “Speciation” of the CETAMA a round-robin modeling exercize was conducted about the U(VI) speciation in waters of known compositions. The objectives were: i) to test thermodynamic data bases; ii) to compare the modelers’ methods in selecting data; and iii) to evaluate the effect of inorganic species on the U(VI) speciation and solubility.

A recent experimental study on the speciation of uranium in drinking waters have shown that calcium uranium carbonato complexes play an important role [1]. The modeling exercize was build on the basis of water compositions of two of these samples. Other water compositions were derived from these in order to better check U(VI) speciation changes with the bicarbonate content, the saline content and [Ca²⁺] and [Mg²⁺]. The participants of this exercize were asked to provide the distribution of soluble uranium species and evaluate the uranium solubility-controlling solid phase for each water. The main outcome is on the importance of alkaline earth carbonate ternary complexes such as Ca₂UO₂(CO₃)₃(aq), CaUO₂(CO₃)₂⁻ and MgUO₂(CO₃)₂⁻. These species were reported in recent publications [2], but rarely included in available data bases. As a consequence it emphasizes the necessity of continuous enrichment of data bases with a consistent approach to avoid bias. Moreover, the amount of uranium in solution could be calculated considering various solubility-controlling phases though such estimations definitely requires the expertise of the geochemist.

In situ U-Th-He dating by \(^4\text{He}/\text{\(^3\text{He}\)}\) laser microprobe analysis

PIETER VERMEESCH AND JAMES SCHWANETHAL

We have developed a rapid, flexible and robust method for in-situ U-Th-He dating, in which (a) multiple zircons from the sample are packed together with a standard of known U-Th-He age, (b) these are proton-irradiated to produce spallogenic \(^3\text{He}\), (c) the grains are ablated with a UV laser once to measure the \(^4\text{He}/\text{\(^3\text{He}\)}\) ratios on a noble gas mass spectrometer, and a second time to measure the \(^232\text{Th}/\text{\(^29\text{Si}\)}\) and \(^238\text{U}/\text{\(^29\text{Si}\)}\) ratios by ICP-MS. The age of the sample is calculated by comparing the measured isotope ratios of the sample to those of the standard (d), and multiplying the resulting 'scaling factors' (f_U, f_Th, and f_He) with the normalised (U, Th, He) composition of the standard (e), which can be calculated from the measured U/Th ratio and its age. This method removes the need to know any absolute concentrations or pit volumes and is immune to ICP-MS matrix effects and collateral laser melting.

Thermal history of a Neoproterozoic orogen and A-type leucogranites formation (Yenisey Ridge, Western margin of the Siberian Craton)

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Integrated geochemical, petrological and numerical modeling investigations allowed to understand the sequence of thermal events that took place during the formation of Neoproterozoic A-type leucogranites located in the structure of the Yenisey Ridge orogen, south-western framing of the Siberian craton (Vernikovsky et al., 2011; Vernikovskaya et al., 2013). Two stages of leucogranite formation were distinguished: 1) 750–720 Ma, and 2) 710–630 Ma. The early stage A-type leucogranite plutons are enriched in potassium and were emplaced (± 10 km) in the Central Angara terrane during the final phase of its collision with the Siberian craton. This collision was followed by the subsequent accretion of the Yenisey island arc to the Siberian craton in an active continental margin setting during 710–630 Ma. At this time the second stage leucogranite plutons were formed at a shallower emplacement depth (± 7 km) within the Tatarka-Ishimba suture zone that was characterized by an elevated heat flow. These leucogranites associate with carbonatites and are characterized by niobium enrichment. The thermal history of the orogen was conditioned by radiogenic heat from the intrusions and their overlapping thermal fields, as well as by elevated heat flow in the suture zone.


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Pleistocene and Holocene temperature reconstructions using earthworm-produced calcite

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Although not widely appreciated, many earthworm species are true biomineralisers, producing calcium carbonate (predominantly calcite) granules in specialised glands [1,2]. Granule production in European soils is dominated by two earthworm species, *Lumbricus terrestris* and *L. rubellus*. By means of laboratory experiments, using a wide range of temperatures (3–20 °C) and water compositions, we have established an oxygen-isotope (δ18O) palaeothermometer for *L. terrestris*. Granules produced by this species are consistently enriched in 18O by 1.5‰ in comparison to equilibrium [3]. Well-preserved earthworm granules are commonly found in archaeological finds and buried soils up to at least ~2 Ma old. In combination with direct U-Th series dating they offer the potential for accurate temperature reconstructions for specific Quaternary time windows.

A selection of earthworm granule samples have been analysed for δ18O values and U-Th composition. The samples originate from several interglacials and interstadials (e.g. Weichselian, Hoxnian, Gelasian), as well as Holocene intervals and well-known archaeological sites (e.g. Silbury Hill, Boxgrove). Temperature reconstructions yield credible values. They show considerable intra-sample variation, which is probably a reflection of seasonal temperature variations. In addition, clear differences can be distinguished between different time intervals. Results will be discussed in context with existing climate reconstructions. We argue that δ18O values of earthworm-produced calcite granules provide a useful and reliable terrestrial proxy for palaeotemperature reconstructions.


2000 yrs of central Mediterranean change – what do proxies tell us?

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The Mediterranean is extremely vulnerable to climate warming through decrease of the critical precipitation-evaporation (P-E) balance. Despite its relevance for society and environment, the natural dynamics of this balance and the human influence thereupon are poorly understood, especially on decadal to millennial time scales.

To increase this understanding we analysed the coastal sediments of the eastern Gulf of Taranto and the Adriatic Mud Belt. The high sedimentation rates, low bioturbation and excellent tephra, 14C, 137Cs and 210Pb and XRF-core scanning-based regional age model allow reconstruction of terrestrial and marine dynamics with a subdecadal resolution.

We present lipid, dinoflagellate and foraminifera-based environmental reconstructions focusing on temperature, the hydrological cycle and human impact during the last two centuries, the Little Ice Age and the Roman Optimum.

The process of regional proxy calibration appeared challenging, not in the least due to having multiple proxies for the “same” environmental variable such as SST (Fig. 1), terrestrial input or productivity. This forced us to reconsider established proxy-environment relations – their accuracy and what they stand for – strongly improving them as sources of knowledge on past environmental change.

Figure 1: SST: one region, different proxies.
The myth of a highly heterogeneous Hf-Nd Eoarchean mantle and large early crustal volumes

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One of the most fundamental and long-standing problems in Earth Sciences is the question of continental growth. Despite decades of work on this problem there is still no consensus on when the continents formed, what were the mechanisms of their formation, and how they have evolved through time. Resolution between the competing models requires insight into the earliest Earth, but the window into this critical time period is far from clear.

One reason for this uncertainty is the lack of old rocks in the geologic record. Crust older than 3.5 Ga constitutes less than 2% globally and the crust that remains is often a complicated mixture of components with different ages and isotopic compositions. Without an accurate integration of age and isotopic composition, analysis of these complicated rocks can yield meaningless information about Earth evolution.

Our solution is to integrate age and Hf isotope data from zircons of the Earth’s oldest rocks. We do this using the laser ablation “split stream” technique whereby the aerosol from the zircon laser ablation is split to two mass spectrometers: one to determine U-Pb ages and the other to determine its corresponding Hf isotopic compositions. In this way we can unambiguously determine age and Hf isotopic composition on the same zircon volume.

Using this approach we find that the isotopic record for rocks older than 3.5 Ga is much less variable than has been recently claimed. Two features stand out from these data. First, there are very few samples with $\varepsilon_{Hf}$ values significantly above zero prior to 3.5 Ga, indicating the lack of a widespread depleted mantle before 3.5 Ga. Second, while there are negative $\varepsilon_{Hf}$ values for some ancient zircons, consistent with recycling of early-formed crust, the lack of a complementary depleted mantle reservoir from 4.4 to 3.5 Ga indicates that the volume of this early enriched (not necessarily continental) crust was modest. We conclude that widespread continental crust formation did not begin in earnest until ca. 3.5 Ga. This is consistent with both the preserved crystalline rock record and the ages of detrital zircons in the sedimentary record.

Hydrogeochemical study of the multi-aquifer system of the Sibari Plain (Calabria, Southern Italy)

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The groundwaters hosted in the Sibari Plain multi-aquifer system are heavily exploited through a large number of wells drilled for agriculture. Similar to many other coastal areas, this excessive groundwater extraction has led to intrusion of seawater. To understand the extension of this phenomenon and adopt suitable actions, a multidisciplinary approach was applied in this investigation, which is carried out in the framework of a PON project: “Study for the environmental protection and the mitigation of anthropogenic pollution in the coastal environment of selected areas of Calabria”.

Hydrostratigraphic correlations, water level measurements, field determinations (electrical conductivity, temperature, pH) and laboratory chemical and isotopic analyses were carried out for 100 selected wells. In particular, high conductivity values, even $>4$ mS/cm, and high chloride contents, up to 1,200 mg/l, were measured in several groundwater samples (Figure 1). Interpretation of geochemical data is complicated by both the dissolution of Miocene evaporite deposits, which generates aqueous solutions with characteristics similar to those dictated by seawater ingression, and the occurrence of other processes, such as bacterial sulfate reduction and ion exchange [1, 2].

Figure 1. Map of $\mathrm{Cl}^-$ concentrations in the wells of the study area and triangular diagrams of major anions and cations.

The role of alkalis in the solubility of $\text{H}_2\text{O}$ and $\text{CO}_2$ in silicate melts

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Solubility experiments were performed on phonotephritic compositions in order to investigate the role of alkalis in the behavior of water and $\text{CO}_2$ in magmatic systems. The investigated melt compositions are based on natural phonotephrite from Alban Hills (Ab1) with Na$_2$O/K$_2$O (in wt %) = 0.26. Two additional compositions with different Na$_2$O/K$_2$O ratios, Ab2 (Na$_2$O/K$_2$O=0.98) and Ab3 (Na$_2$O/K$_2$O=3.82), were synthesized. Experiments were run at 1250°C and 500 MPa in an internally heated gas pressure vessel. The proportions of water and CO$_2$ in the systems were systematically varied in the range from 0 to 1. For the calibration of carbon-related IR bands, the total carbon content of the synthesized standards was measured by combustion and subsequent IR spectroscopy using an ELTRA CS800 analyzer. Karl Fischer Titration method was used in order to quantify H$_2$O content in the melts. Absorption spectra were recorded in the mid-infrared (MIR) using a Bruker IFS88 FTIR spectrometer coupled with an IR-Scopell microscope.

CO$_2$ is bound in the investigated glasses as CO$_3^{2-}$ exclusively and its concentration was quantified by the peak height of the 1430 cm$^{-1}$ band. A drastic change was observed in the absorption coefficients, $\epsilon$, with values of 265 ± 27.2, 228 ± 22.4 L/(mol·cm) and 308 ± 26.6, for Ab1, Ab2, and Ab3, respectively, so that the highest $\epsilon$ value is related to the Na-rich composition. There is no detectable effect of the Na/K ratio on the concentrations of dissolved H$_2$O and CO$_2$ in the melts. The solubility of CO$_2$ and H$_2$O in those melts at 500 MPa is 1.2 wt % and 10.07 wt%, respectively. Results are compared with the existing literature data and models and confirm the very high solubility of CO$_2$ in phonotephritic melts [1]. Our experimental data indicate that the melt composition in terms of alkali contents influences significantly the extinction coefficient values for CO$_2$ and that appropriate coefficients must be selected to estimate accurately the amount of dissolved CO$_2$ in glasses and/or melt inclusions using IR spectroscopy.


Magma droplets in coexisting olivine and spinel phenocrysts hosted in the Pohang basalt (South Korea)

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Primary silicate melt inclusions (SMI) in different host minerals provide a unique possibility to reconstruct the evolution path of the host magma. The 2 million years old Pohang alkaline basalt from South Korea contains such silicate melt inclusions hosted in olivine and spinel phenocrysts.

The Pohang basalt has porphyritic texture and contains forsteritic (mg#=0.84-0.88) olivine, Cr-bearing (cr#=0.15-0.24), high Mg (mg#=67.0-69.0) spinel phenocrysts and anorthite-rich plagioclase. The microphenocrystal groundmass consists of olivine, clinopyroxene, spinel, plagioclase and glass. Olivine and spinel phenocrysts have negative crystal shaped or rounded SMIs in size up to 150 microns in diameter. These magma droplets are identified in zoned clinopyroxene, Al-Mg-rich spinel, K-Na-Si-Al-rich residual glass, Ni-Fe-rich sulfide blebs and bubble(s). In addition, olivine daughter minerals occur in the spinel hosted SMIs.

Based on the results of homogenization experiments (with heating-quenching technique) and the equilibrium temperature calculated from olivine-spinel pairs, the homogenization temperatures are in the range of 1050-1240°C in the SMIs irrespectively their host minerals. The estimated oxygen fugacity values are -1.810 to -0.942 log units below the fayalite-magnetite-quartz buffer indicating SMIs entrapment from a relatively reduced magma. Based on geochemical data, it is suggested that the SMIs in both host minerals were entrapped at the very early stages of the crystallization process and it shows the same crystallization sequence: spinel, olivine, sulfide blebs, clinopyroxene, residual glass and bubbles.

The REE patterns of SMIs are flat or slightly decrease from La to Lu, with (La/Lu)N between 1.6 and 17. The low La/Y and Zr/Nb ratios suggest spinel lherzolite source rock for the Pohang basalt.

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Accumulation of trace elements in the Lake Baikal biota

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The objective of the work was to assess accumulation of chemical elements by different hydrobionts' species and to find out a role of biota in removing trace elements from the lake water. Contents of about 30 trace elements were studied in 1979–1987 in plankton, benthos species (hammaridae, polifera, molluscs), most common food fish and in Baikal seal. The full set of AE-, AA- and NA-analytical techniques was used.

Accumulation factors (AF, the ratio of element concentration in dry tissue to that in water dry residue) for 28 metals (Na, Al, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Hg, Pb, Th, U) and Br showed that there was no regular rise of a metal concentration in dry biomass when going from an initial producent (phytoplankton) up to ultimate consument (seal). From all 29 considered elements only Rb revealed a tendency to increasing bioavailability from lower trophic levels to upper ones. As a rule, changes in AF’s for other elements do not show any certain regularity depending on trophic levels.

The following metals have highest AF: in phytoplankton (AF > 30) – Al, Fe, Pb; in zooplankton (AF > 10) – Al, Fe, Cd, Ce, Hg, Pb; in molluscs (flesh, AF > 100) - Al, Mn, Fe; in seal (flesh, liver, AF > 50) – Al, Fe, Cd. Metal accumulation in fish tissues is relatively low, AF exceeds 5 only for Al, Mn, Fe, Ce.

Estimates of metal flux rates to bottom sediments were calculated on the basis that the input of autochtonic organic matter to sediments was equal to 800,000 ton/year resulting mainly from phytoplankton annual primary produce. These flux rates should be considered as semi-quantitative major estimates which just indicate that uptake of some metals (Na, Cr,u, Zn, Sr, Ag, Cd, Sn, Sb, Hg, Pb, U) by phytoplankton can be a significant route to their removal from the waterbody to the bottom sediments.

Monitoring the stability of scale inhibitors by ATR-FTIR at high pressures and temperatures in synthetic geothermal fluids

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Mineral precipitation (scaling) such as sulfates, carbonates, and oxides are well known phenomena in geothermal plants. These precipitations damage plant equipment (e.g. heat exchangers) or reduce the injectivity of the reservoirs and thus the operation lifetime of such installations. In this context, the use of environmental friendly inhibitors to avoid the formation of these mineral precipitations become attractive.

In this study, scale inhibitors based on ecologically harmless polycarboxylates are examined with respect to their thermal stability by attenuated total reflection - Fourier transform infrared spectroscopy (ATR-FTIR). The spectroscopical device is equipped with a high pressure - high temperature reaction cell that allows measurements at up to 200 °C 200 bar. In this study, changes in signal intensity and band position for various inhibitors were monitored dependent on temperature and pressure. Additionally, the behavior of scale inhibitors in synthetic fluids at different ionic strengthes (up to 5M NaCl) is evaluated as a function of temperature and pressure.
Sulfosalt melts from low-grade metamorphic terrains: The case of the Monte Arsiccio mine (Tuscany, Italy)

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Sulfosalt melts formed during amphibolite/granulite facies metamorphism of pre-existing orebodies have been well documented (e.g., [1]). However, orebodies containing significant amounts of Low Melting Point Chalcophile Elements (LMCE - Ag, As, Bi, Hg, Se, Sb, Sn, Tl, and Te), could experience sulfosalt/sulfide melting at much lower metamorphic temperatures [2]. Up to date, low temperature LMCE sulfide melts have been documented, as inclusions in quartz, only at Lengenbach, Switzerland [3].

A new interesting case study was provided by the barite-pyrite-iron ore deposit from Monte Arsiccio (Apuan Alps, Tuscany, Italy). The deposit originated during a Palaeozoic-Triassic sedimentary-exhalative metagenetic event and was successively metamorphosed and remobilized during the Alpine orogeny [4] under greenschist facies conditions (P = 0.6-0.8 GPa, T = 350-450°C; [5]).

Within these orebodies we discovered an exceptional Tl-Hg-As-Sb-(Ag, Cu)-Pb sulfosalt assemblage embedded in the barite-pyrite ore and in dolostones. Mineralogy is dominated by LMCE-bearing phases, mainly represented by Tl-Hg-Sb-As sulfosalts. The textural features of these assemblages (tiny veinlets pierced along grain boundaries, drop-like internal textures, low interfacial angles between sulfosalts and matrix mineral grains) is interpreted as the result of the mobilization of low-viscosity sulfosalt melts by percolation through the barite-pyrite crystal matrix, and veining in dolostones. Experimental studies (e.g., [6]) support our hypothesis, showing that thallium-bearing polymetallic sulfide systems could experience sulfosalt/sulfide melting at much lower metamorphic temperatures.

Magma emplacement and sulfide deposition after skarn formation at Campiglia Marittima, Tuscany

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Most economic skarn deposits are related to magmatic intrusions and a general correlation exists between the composition of igneous rocks and skarn ore type [1]. The Cu-Pb-Zn-Ag skarn deposit of Campiglia Marittima (Southern Tuscany, Italy) is the skarn deposit in which a mineralogical zoning of skarn bodies has been first described [2]. It has been considered as a classic example of exoskarn with an outward zoning sequence developed from a main axial dyke of mafic porphyry: magnetite ⇒ ilvaite ⇒ clinopyroxene ⇒ marble [3]. According to this model, the skarn deposit of Campiglia Marittima represents a key example for the understanding of the spatial and temporal evolution of a metasomatic system, from the local source of ore fluids (mafic porphyry) to the final products (skarn and sulfides).

The new field and laboratory data collected for Campiglia Marittima skarn deposit indicate that this classical model is too simplistic. Geological mapping of about 20 km of tunnels/shafts shows that: 1) mafic porphyry does not form a single axial dyke but small dykelets and pods that crosscut the skarn bodies and fill the skarn pockets; 2) the skarn bodies do not show symmetric, outward growing, mineralogical zoning, but they are formed by several metasomatic units displaying distinct mineral parageneses and growing patterns.

The later intrusion of mafic porphyry heated up the skarn bodies, inducing significant prograde back-reactions on skarn minerals: 1) ilvaite in direct contact with mafic porphyry was replaced by magnetite + hedenbergite; 2) pyrophyte, pyrite and chalcopyrite variably replaced ilvaite for several meters from the contacts; 3) hedenbergite crystals suffered overgrowth of Mg-rich rims.

Thus, a direct causality between magma emplacement, fluid release and skarn/ore formation, at a local scale, is not confirmed and must be searched at a larger, crustal scale. The magmatic source of skarn fluids is inferred to be a deeper, mafic intrusion. The shallow level of emplacement of such intrusion controlled the early exsolution of skarn fluids, and the later extraction of magmas that fed the mafic porphyry system, forming the main sulfide ores.


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Influence of tectonics on magma residence times at Mt. Etna volcano

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Trace element zoning in plagioclase from the historic (pre-1971 AD) and recent (post-1971 AD) activity of Mt. Etna volcano was here used to evidence changes in the feeding system dynamics during the last 250 years. The observed textural characteristics of crystals include both near-equilibrium and disequilibrium textures [1]. The An variation along core-to-rim profiles on selected crystals with different types of textures was evaluated particularly versus the Sr/Ba ratio. At rather comparable average An contents, plagioclase crystals representative of near-equilibrium crystallization from the magma display very distinct Sr/Ba ratios through time (~6 and ~17 in historic and recent lavas respectively). Recent plagioclases also exhibit generally higher potassium contents than the historic ones at the same evolutionary degree. Although contamination due to wall-rock assimilation may have played a role, we suggest here that the features are dominated by input of a K-rich and Ba-poor end-member into the feeding system that becomes evident particularly after the 1971 AD eruption. Magma residence times, which have been calculated through Sr diffusion modeling on plagioclases, are longer by a factor of ~40 years for crystals of the historic activity and ~20 years for the post-1971 AD plagioclases. Our estimations strongly agree with geophysical data that highlight an increased E-W directed extension rate within the upper 10 km of the crust before major eruptive events of the last two decades. Differences in the timescales of magma storage observed over the last 250 years can be therefore attributed to the dominant role played by volcano-tectonics on the uppermost part of the feeding system.


Insights into the magmatic processes leading to the Holocene caldera eruption of Rinjani, Indonesia

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The cataclysmic caldera-forming eruption at Rinjani volcanic complex (Lombok, Indonesia) ranks among the largest explosive eruptions of the Holocene, and is possibly associated to the largest stratospheric release of volcanic sulfur over the past 7 ka [1]. It produced a succession of plinian fallout and pyroclastic flow deposits. Whole-rock analysis of juvenile pumices from plinian fallout units indicates a range of trachyandesitic to trachytic magma batches (61-64 wt% SiO_2). These magmas display variable enrichments in both major and trace elements indicative of a dominant process of crystal fractionation and of the presence of a zoned (or complex) magma chamber. They also share Nb/Th (0.9) and Nb/Zr (0.04) ratios with those of Rinjani high alumina basaltic scoriae, suggesting that they belong to the same suite. As a whole the compositional range of our samples matches that of the Rinjani calc-alkaline suite [2].

The mineral paragenesis consists of plagioclase (An_41 to An_80), clinopyroxene (Mg# 0.75), orthopyroxene (Mg# 0.71), amphibole (paragasic Hbl/magnesio Hbl) and Fe-Ti oxides. Biotite is rarely found. Apatite shows a wide range of volatile contents: F 1.8-0.25 wt%, Cl 0.9-0.45 wt% and S 1300-<100 ppm. Melt inclusions analyzed in plagioclase handpicked from a basal fallout unit represent the most evolved trachytic term (65-70 wt% SiO_2, on anhydrous basis). They contain 3.3-5.1 wt% of H_2O, 2200-3700 ppm of Cl, 440-600 ppm of F, and <100-490 ppm of S. CO_2 is below FTIR detection limit. The erupted magma was thus rich in H_2O and Cl but relatively depleted in sulfur. The estimated P_{H_2O} for this range of water contents is 180-100 MPa [3] that is consistent with prolonged magma ponding at crustal level.

We provide the very first constraints on the pre-eruptive magma conditions and discuss the processes controlling sulfur behavior.

Dissolved mercury in Funil reservoir, RJ, Brazil

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Introduction

Diffuse emissions of several contaminants are linked to water and energy, as the need for these leads to modification of frequency, magnitude and nature of the contribution of water and sediments, mainly due to interventions in the drainage basins such as the reservoir formation. Among these contaminants is mercury (Hg), which offers known health risk [1]. Therefore, this study evaluated the effect of the Funil dam, located in Resende, RJ, SE Brazil, in the level of Hg dissolved in water at three points of the Paraíba do Sul River (RPS) during 1 year.

Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>ago/10</th>
<th>set/10</th>
<th>out/10</th>
<th>nov/10</th>
<th>dez/10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upstream</td>
<td>1.38</td>
<td>0.15</td>
<td>0.13</td>
<td>1.60</td>
<td>1.65</td>
</tr>
<tr>
<td>Reservoir</td>
<td>0.59</td>
<td>0.08</td>
<td>&lt;0.05</td>
<td>4.58</td>
<td>0.23</td>
</tr>
<tr>
<td>Downstream</td>
<td>0.87</td>
<td>0.11</td>
<td>0.16</td>
<td>3.28</td>
<td>1.61</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>fev/11</th>
<th>mar/11</th>
<th>abr/11</th>
<th>jun/11</th>
<th>jul/11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upstream</td>
<td>5.00</td>
<td>2.70</td>
<td>10.12</td>
<td>2.49</td>
<td>1.16</td>
</tr>
<tr>
<td>Reservoir</td>
<td>3.02</td>
<td>4.55</td>
<td>4.92</td>
<td>1.11</td>
<td>26.42</td>
</tr>
<tr>
<td>Downstream</td>
<td>9.44</td>
<td>1.87</td>
<td>2.64</td>
<td>3.12</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Figure 1: Hg concentrations in Paraiba do Sul river (ng.L⁻¹).

Samples showed concentrations below the maximum allowed by law [2]. Although the basin RPS has compromised quality of water in several parts, this region does not suffer significant contamination by the element studied.


Hydrogeochemical characteristics of water source in the area of Lazarevo village (from the aspect of balneology)

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Geological data obtained from boreholes for oil and gas were used for geological mapping of “Jaša Tomić” sheet 1:100,000, in the area of Pannonian basin represents a special geothermal province (M. Milivojević, 1989) and one complex hydrogeothermal conductive system with four mutually separated reservoirs of underground water. A first hydrogeological system includes Upper Pontian sediments about 2 km thick in Northern Banat and a few tens of meters in peripheral parts of the basin. In deeper parts clayey-marly sand prevail. In shallower parts larger parts presence of sandy-pebbly sediments of lacustrine and river origin are dominant. Sand water-bearing sediments parts presence vary from 1 to 50 m in thickness. The source of mineral water is located nearby structural boreholes Lazarevo (La-1), Topolovac (Tc-1) and borehole for water supply of village Lazarevo.

<table>
<thead>
<tr>
<th>HCO₃</th>
<th>SO₄</th>
<th>Cl</th>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>Ca</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>569</td>
<td>3655</td>
<td>2744</td>
<td>3076</td>
<td>273</td>
<td>286</td>
<td>118</td>
<td>20</td>
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<tr>
<td>1464</td>
<td>2120</td>
<td>459</td>
<td>1740</td>
<td>1</td>
<td>101</td>
<td>69</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 1: Physical-chemical composition (mg/l) of mineral water in Lazarevo (well) – First raw – data from 1957; second raw – data from 2012

According to results of laboratory researches (2012) water is medium mineralized low alkaline subthermal, Na-Mg-Ca, SO₄-HCO₃-Cl which classifies it as low alkaline saline bitter water. Water which was analysed in the period of 1957 belongs to medium mineralized low alkaline type of water, Na-Mg-Ca, SO₄-Cl-HCO₃ which classifies it as saline-muriatic-bromine-bitter water which is very healing. Variations in chemical composition are obvious, and they depend on the regime of underground water and aquifer type. Reseraches related to this are planned in the following period.

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Hf-Nd isotope decoupling in Early Precambrian seawater

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Banded Iron Formations (BIFs) are Precambrian marine chemical sediments that are archives of the trace element and isotope compositions of ancient seawater. Here we report Hf and Nd isotope data of pure chert and magnetite layers from the ca. 2.7 Ga Temagami BIF (Superior Province, Canada), determined by isotope dilution techniques and MC-ICPMS. Sample aliquots were also analysed for trace element systematics by quadrupole ICP-MS.

Shale-normalised REY patterns of the BIFs are similar to those of modern seawater and other pure Archean seawater precipitates. Enrichment of HREE compared to LREE, positive La and Gd anomalies, and super-chondritic Y/Ho ratios indicate a purely seawater-derived REY composition. Lacking Ce anomalies and strong positive Eu anomalies reveal anoxic conditions (with respect to Ce⁴⁺/Ce³⁺) and REY input into seawater via high-T hydrothermal fluids. Non-chondritic Zr/Hf ratios indicate minor influence of detrital aluminosilicates and a seawater origin of Hf. Samarium-Nd and Lu-Hf isochron ages are within error of the published depositional age of the ~2.7 Ga Temagami IF. Initial εNd2.7Ga values range from +0.2 to +3.0, but six of the nine samples cluster around +1. In contrast, initial εHf2.7Ga values point towards heterogeneous, strongly radiogenic compositions (+6.7 to +24.1). In the εHf-εNd diagram, the Temagami BIFs lie well above the `terrestrial array´ and exhibit significantly different εHf-εNd values than Temagami shale and hinterland tholeiites and adakaites which tapped the Abitibi mantle [1].

Therefore, Temagami seawater Hf was even more radiogenic than ambient mantle, suggesting that selective weathering processes (including the zircon effect) already operated in the Neoarchean, leading to the decoupling of the Hf-Nd isotope systematics, that is well known from modern seawater [2] and Cenozoic FeMn precipitates [3]. This suggests that by 2.7 Ga ago, a significant fraction of evolved continental crust was exposed above sealevel and subject to terrestrial weathering.


Zn isotope fractionation in pristine larch forest developed on permafrost-dominated soils in Central Siberia

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Towards a better understanding of Zn transport and storage in the tree-soil-mineral-river system, stable Zn isotope fractionation was studied in main biogeochemical compartments of a pristine larch forest of Central Siberia developed over continuous permafrost basaltic rock lithology.

It appears that Zn isotopes are not fractionated within the soils compared to the basaltic rocks. By contrast Zn isotope fractionation is observed between plants (larch) and soil and within the plant itself. Among the different habitats of the region receiving different amount of solar radiation and nutrients (South- and North-facing slope, peat bog) we observe systematic habitat-specific differences of Zn isotopic composition between whole plant and soil. As there is no apparently different physiological behavior of Zn within the same species within the different habitats we suggest the key role of Zn speciation in the soil solution to explain these differences.

We observe a change of Zn isotopic composition in the larch needles within the course of the growing period suggesting a change in the nutrients source. Although the isotopic measurements do not allow distinguishing between mineral and organic source of Zn in natural waters, it can be concluded that, within the climate evolution and the increase of the thickness of thaw layer in peat bog environments, the global value of δ⁶⁶Zn in Siberian larch forest will increase.


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New constraints on K-Pg boundary environmental changes with Li isotopes

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Climatic and oceanic perturbations associated with the Deccan Traps eruption and with the Chicxulub impact are still strongly debated. Because lithium isotopes significantly fractionate during low temperature processes, the composition of mineral phases formed across the K-Pg boundary can provide quantitative information concerning environmental changes at that time. In this study, we investigate in parallel the Li isotope composition of both marine authigenic smectite and benthic foraminifera over a time window of 3 Ma. Comparing both phases is important because the $^{7}\text{Li}$ of foraminifera may be subject to vital effects during calcification, while authigenic clays are not. The objectives are: 1/ To determine the long-term variation of seawater $^{7}\text{Li}$ due to changes in continental flux and alteration rate and 2/ To detect short-term variations of the ocean carbon chemistry, recorded by Li isotope fractionation during foraminifera growth.

Li isotopes are measured in clays by MC-ICP-MS, and in benthic foraminifera tests using the ims 1280 ion microprobe, at University of Hawaii. Initial results show a limited variation ($\leq 2\%$) of clay $^{7}\text{Li}$ across the Ir-rich layer, indicating little disturbance of the ocean Li at that time. Compared with 0-6 Ma seawater, K-Pg seawater $^{7}\text{Li}$ was 5.5$\%$ lower, suggesting a lighter input from continents due to more intensive and more congruent continental alteration.

In contrast, contemporaneous benthic foraminifera tests vary significantly on time scales much shorter than the oceanic residence time of Li (1-1.5 Ma), too short to attribute to changes in the $^{7}\text{Li}$ of the global ocean. Also, these variations precede deposition of the Ir-rich layer. These results strongly suggest changes in Li isotope fractionation through time. The $^{7}\text{Li}$ of cultured foraminifera indicate a strong dependency on the DIC concentration, but no impact of pH and T on Li isotope fractionation during foraminifera growth. If these data are representative of natural conditions, then our results indicate significant short-term oscillations of ocean DIC before Chicxulub, possibly related to eruption events in the Deccan.

Wild rats as sentinel animals in the assessment of asbestos pollution: a pilot study

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Asbestos fibres are potential carcinogens to humans when reach lungs. Animals can be served as sentinels being exposed like humans to contaminants. Recently investigations on the asbestos burden to evaluate the exposure level in the environment has been successfully carried out on cows [1]. To investigate in towns where these animals don’t live, rats as diffused species can be considered. Rats live in colonies in a circumscribed territory. The use of rats as “sentinel animals” would allow to carry out an innovative monitoring method with important practical applications. The aim is to identify the neighbourhoods of the city at risk, by searching for asbestos fibres in the lung tissue of wild rodents captured in specific areas of the Casale Monferrato town. Three kinds of asbestos (crocidolite, chrysotile and asbestos tremolite/actinolite) and five groups of non asbestos fibres (metallic oxides; Al-, Ti- and vitreous silicates; phyllosilicates) have been detected in the rat lungs by SEM-EDS investigations. These data together with that obtained from positive and negative control rat lungs showed rats are suitable sentinel animals to detect air dispersion hidden sources of asbestos and other inorganic fibres. Regarding the studied area, crocidolite and asbestos tremolite/actinolite are related respectively to anthropogenic and natural sources. Therefore a complete investigation would allow to identify sites of noxious inorganic phase potential dispersion in order to adopt tools to contain or eliminate it before the general population can be damaged.


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Hydrogen mobility in Wadsleyite at low temperatures

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Mantle wadsleyite may incorporate large amount of H in its structure (up to several wt % H2O). A good knowledge of hydrogen diffusion in wadsleyite and its relationship with electrical conductivity is critical to estimate the amount of water present in the transition zone. We present here the results of diffusion experiments realized in deuterium-rich atmosphere at room pressure between 300°C and 450°C. Wadsleyite samples have been synthesized from forsterite powder with a minute amount of water by multi-anvil presses at 16 GPa- 1100°C. The average grain size is less than 5 µm and the water content is around 0.01 wt% H2O. All samples show major IR peaks at 3372, 3350 and 3322 cm-1 with minor peaks at 3726, 3665, 3615, 3523, 3472 and 3208 cm-1.

We observed the same OH extraction behavior in the three slides annealed: extraction kinetics of bands 3726, 3523, 3372 and 3208 cm-1 is almost 100 times slower than other bands while deuteration affects all the bands in the same way. We obtain an activation energy of 175 kJ/mol for extraction of the “fast” decreasing bands and an activation energy of 202 kJ/mol for H-D exchange.

Our data extrapolated to high temperatures suggest that hydrogen mobility in Mg-wadsleyite is two orders of magnitude higher than extraction kinetics from Hae et al. (2006) (D=8.3×10-11 m2/s at 1000°C) or it implies a concentration of hydrogen two orders of magnitude smaller.

**Observations and modeling of sinking particle speeds in the Twilight Zone using $^{210}$Po-$^{210}$Pb deficit**

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2Universidad Pablo de Olavide, Dpto. Sistemas Físicos, Químicos y Naturales, Sevilla, Spain
3Department of Ocean Biogeochemistry and Ecosystems, National Oceanographic Centre, Southampton, UK

A one-box model of $^{234}$Th uptake and removal in the water column is widely used to calculate downward $^{234}$Th and POC flux. The elemental pair of $^{210}$Po-$^{210}$Pb is an alternative method to estimate carbon fluxes which should offer significant advantages due to its different half-life (138 days) and biogeochemical behaviour. Due to its long half-life, a $^{210}$Po deficit is maintained below the euphotic zone and penetrates much further into the twilight zone (100-1000 m) than $^{234}$Th. Hence $^{210}$Po and $^{210}$Pb profiles and $^{210}$Po deficit could be used to broaden our knowledge of the twilight zone.

To address this question several water column profiles were sampled during two expeditions of RSS Discovery on the North Atlantic, PAP site (summer 2009) and Irminger Basin (summer 2010). The most important contribution of this work is that $^{210}$Po activity down the water column is modelled using a one-box inverse model. Modelled $^{210}$Po activities are in very good agreement with the analysed values and the new approach provides information to understand $^{210}$Po and $^{210}$Pb concentration profiles on the water column. A key output from the model is average downward sinking velocities. Minimum and maximum values range from 20 m·d$^{-1}$ at 50 m to 150 m·d$^{-1}$ at 400 m. Averaged values at PAP and Irminger areas do not follow a clear geographical pattern; however, an increase with depth is observed. Finally, the contribution of slow sinking particles into the twilight zone and its implication to the carbon storage is discussed.

**Adsorption experiments of arsenic and lead onto barite**

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The work consists in the study of the retentions of arsenic and lead onto the barite surface. The barite sample is from a deposit of Múzquiz (Coahuila, México). The batch adsorption experiments using salts of As(III), As(IV), and Pb(II) was according [1]. A measurement of the pHpzc of the barite sample was determined by acid-base titrations.

<table>
<thead>
<tr>
<th></th>
<th>As(V)</th>
<th>As(II)</th>
<th>Pb(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH adsorption</td>
<td>8.35</td>
<td>8.55</td>
<td>8.45</td>
</tr>
<tr>
<td>C$_{0}$ (mg/L)</td>
<td>5.92</td>
<td>9.69</td>
<td>7.07</td>
</tr>
<tr>
<td>C$_{24h}$ (mg/L)</td>
<td>5.08</td>
<td>9.67</td>
<td>&lt; L.D.</td>
</tr>
<tr>
<td>Adsorption %</td>
<td>14</td>
<td>0.17</td>
<td>100</td>
</tr>
<tr>
<td>R$_{d}$ (mL/g)</td>
<td>3.6</td>
<td>0.04</td>
<td>2951</td>
</tr>
</tbody>
</table>

Limit of detection (L.D.) for lead is 0.05 mg/L

Table 1. Results of the adsorption experiment. The adsorption was calculated taking account the concentration of the dissolved species. Calculation of the distribution ratio ($R_{d}$) between the solutes and barite mineral was calculated as Griffin et al. [1].

The determination of the pH$_{pzc}$ of the barite is about 9.8. The present study shows that the barite could be used as adsorbent for Pb(II). Although the adsorption of arsenic is lower, is more effective for As(V) than for As(III). At the pH of adsorption the As(III) the predominant species is not charged ($\text{H}_3\text{AsO}_3$), but the As(V) occurs as $\text{HAsO}_4^{2-}$ and can be electrostatically attracted to the positive surface of the barite.

Successive geotherms, Granitic production and evolution of the lower crust in a post collisional context

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Post-collisional context is commonly associated with production of large amount of peraluminous granitic magmas produced from the melting of crustal material. The variability of the produced granite commonly varies from leucogranitic to granodioritic and are mostly peraluminous. The South-Eastern French Massif Central (EFMC) region record several evidence for crustal melting revealed by migmatitic and granitic bodies providing ~30 Ma history of peraluminous granite production. Previous thermobarometric studies provides records for two successivves melting event: 1) a biotite stable event at ~314Ma (720°C and 5 kb)  2) a bitotite breakdown melting event constrained at ~301Ma (850°C 4kb) This suggests geotherms evolution from 45 °C/km to 70°C/km in 13Ma.

A thermodynamic modelling approach considering a 20km thick pile of crustal material undergoing successive geotherm evolving from 25°C/km to 70°C/km with starting conditions between 3 and 10 kb. Along this evolution our approach allows successive melt extraction and the monitoring of melt compositional variability, residuum evolution and mineral phases modal and compositional variabilities according to depth, geotherm and composition of the source.

Over the 5 crustal sources used as starting composition for the model, 305 individual partial melting reactions are triggered. Melt and peritectic phases produced provide a variability that suggest the importance of source composition in matter of granite production for some element and ratios (K/Na, XMg). Compared to regional granites (EMCF). Most of the granites produced in the post collisional context of the EFMC can be reproduced by either melt only (leucogranite) or melt in addition to peritectic material produced along with melt (granite to granodiorite). In the same way, the relative-time constrain provided by the approach shows that it is possible to produce simultaneously heterogeneous granitic magmas in respect to source protolith and depth. Identically, the residual crust undergo an very variable evolution depending on protolith leading to an heterogeneous granulitic lower crust.

Phosphorous Speciation in Atmospheric Deposition Samples in the East Mediterranean

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The interactions between phosphorus-carbon cycles and climate are expected to become an increasingly important determinant of the Earth biogeochemical cycles. The oceans generally act as an important sink of atmospheric CO2. P limitation of marine primary productivity could play a key-role in this natural process, affecting indirectly the global warming. East Mediterranean Sea (EMS) is P-limited and new knowledge could be arisen by defining the role of organic and inorganic forms of atmospheric P deposition into the marine environment.

This study aims to investigate the sources, the forms and the biogeochemical significance of soluble and insoluble atmospheric P over the EMS. Wet (n=55) and bulk deposition samples (n= 76) have been collected during four-year period (2008-2009 and 2011- 2012) and analyzed for P speciation. Following the analytical protocol referred in Standard Methods for the Examination of Water and Wastewater (20th Edition), Total Dissolved acid hydrolized Inorganic Phosphorous (TDIP) was determined after mild oxidation of sample. Total Dissolved Phosphorus (TDP) was measured after the acid digestion of samples according to Persulfate Digestion Method. Dissolved organically bound phosphates (DOP) were determined by subtracting TDIP from TDP. Dissolved Reactive Phosphorous (DRP) was determined as HPO42- with Ion Chromatography (IC).

To investigate the role of air mass origin in the P speciation in rainwater, rain samples have been classified in two classes (N/NW and S/SW) corresponding to the main wind sectors influencing the area. DOP is associated with S/SW winds that enrich the atmosphere over the EMS with African dust. N/NW winds transport anthropogenic pollution from N/NW Europe and are associated mainly with DRP. In addition, P solubility changes have been observed and are analysed.

Dry deposition of P is found to be higher than the wet one and is dominated by DRP that is so far known as the most bioavailable form of P and thus is expected to have singifiincat impact on the marine ecosystems.
Modelling carbon cycle and major cations weathering fluxes in a young temperate forest

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Chemical weathering provides mineral nutrients to the soil solution. The productivity and resistance of the vegetation is dependent to its capacity to find and adsorb these nutrients. The vegetation itself plays an active role in mineral dissolution by the exudation of organic acids. Indirectly, (i) the nutrient uptake can deplete them in the soil solution and (ii) the soil respiration increases the pCO2. Both indirect processes also favour the chemical weathering. In poor acid soils, the fertility relies mostly on the organic matter recycling and/or atmospheric inputs. But the biological cycle is not closed and losses by the run off are unavoidable. Moreover, in a young growing forest, the initial pool of mineral nutrients has to be built.

For 20 years, the chemical composition of the streamwater La Robinette, in the Belgian Ardennes has been monitored. It initially aimed at the estimation of cations losses due to soils acidification and at the understanding of the forest decline. After a large windfall and a clear-cutting in 1995, spruces were replanted and partially replaced by deciduous species.

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Chemostrogratigraphy of Paleoasian ocean’s microcontinent covers

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After the breakdown of the Rodinia super continent the Siberia for a long time was a continent surrounded by the water (700 Ma [1]). The ocean between Siberia continent and others big continent is called Paleoasian ocean. Thick carbonate deposits have been accumulated on Siberia passive border and on the microcontinents surrounding in Ediacarian time. This study about investigation of Sr and C isotopic composition of Ediacaran and Cambrian carbonate covers of following microcontinents: Tuva-Mongolian, Zavkhan (both in Mongolia now), Batenev and North-Muya (Russia).

Based on petrographic and geochemical analyses we identified the least altered rock samples. These samples are thought to have primary Sr isotope composition reflecting that of the paleocean. The least altered carbonates of the Tuva-Mongolia terrane have Sr isotope values of 0.7073-0.7086 and δ13C values alter from -1.7 to +5.0‰ [2]. The primary 87Sr/86Sr ratio for Zavkhan carbonate are 0.7072-0.7079 for Tsagaan Oloom Fm (δ13C vary from +3 to +14‰) and 0.7084-0.7086 for Bayan Gol Fm. Carbonate cover of Batenev microcontinent is characterized by 87Sr/86Sr rations of 0.7075-0.7085 and δ13C is -2.5 …+3.7‰ [3]. The 87Sr/86Sr ratio from North-Muya microcontinent vary from 0.7085 to 0.7086 and it have δ13C about 0.

When compared with the 87Sr/86Sr ratio variation curve [4] it can be seen that the deposits accumulated asynchronously from the early Ediacaria to middle of Cambrian and cannot be used for lithological correlation of the carbonate successions. The work was supported by the RFBR (projects nos. 12-05-00569, 12-05-33076).


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Global lithium deposits (pegmatites and brines) as indicators of plume-tectonics

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Spodumene pegmatites. Comparative analysis of geotectonic position of Li-bearing pegmatite deposits of Central Asian Folded Belt and their isotopic ages (U-Pb, Rb-Sr, Ar-Ar, Re-Os) suggests the coincidence of time intervals of the pegmatite formation with main age peaks of plume activity (LIP). The origination of deep-seated granite sources of the pegmatite melts with extremely high lithium contents was stipulated by asthenosphere uplift, and their occurrences was connected with strike-slip deformations in continental lithosphere [1-2].

Salt lakes. Comparative analysis of lithium brine deposits of South America and Central Asia allowed us to conclude that lithium contents in lake waters were determined by lithium concentrations in feeding springs and underground waters, their salinity, tectono-volcanic activity of considered regions, arid climate conditions. The formation of lithium brines of salt lakes is usually connected with leaching of acid tiffs, entering in bimodal volcanic series, which are characteristic for marginal and within-plate riftogenesis [3-4].

The work was supported by the Presidium of SB RAS (projects № 77, 110, 123), FGP “Research and scientific-pedagogical personnel of innovative Russia” (№ 2012-1.2-12-000-2008-8340).


Siderite Amendment for in situ pH Control in Hyperalkaline Environments

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Remediation of soils and sediments and restoration of sites contaminated by hyperalkaline wastes associated with legacy industrial facilities (e.g. Solvay and chlor-alkali process wastes) present unique challenges and opportunities for geochemical engineering solutions. The feasibility and success of in situ treatment strategies such as soil mixing and sediment capping in such settings depends on the use of reactive amendments that can maintain long-term pH neutralization and ultimately lead to establishment of plants and habitat restoration. We present results of extensive experimental and modeling studies carried out to evaluate the reactivity, kinetics, and performance of siderite (FeCO3) for such applications. Porewater pH neutralization and buffering by natural siderite ore concentrates from Texas was investigated in a series of kinetic batch tests using a hyperalkaline (pH 12) Na-Ca-Cl brine porewater from contaminated lake sediments. In all tests, pH was neutralized and consistently buffered to circum-neutral values within timeframes of weeks to months. The reaction rate was inversely dependent on liquid/solid ratio (varied between 2:1 to 50:1) and only weakly dependent on siderite grain size (from 0.1 to 2 mm), the latter due to the aggregate nature of the siderite ore which consists of individual crystallites <50 μm in size. Calcite and iron oxides/oxyhydroxides were identified as the main reaction products in the batch experiments. Column testing confirmed the effectiveness of siderite for pH neutralization under dynamic flow conditions representative of field situations with groundwater upwelling through contaminated sediments. A reactive transport model of a siderite-amended sediment cap, incorporating time-dependent porewater upwelling and consolidation following cap construction, siderite dissolution (pH-dependent transition-state theory rate law) and secondary product precipitation kinetics, was developed using PHREEQC with reaction rate constants calibrated to the batch experiment data. The model has been used to simulate pH neutralization under different sediment cap designs, conduct sensitivity analyses to assess potential effects of vertical segregation of amendments during subaqueous cap materials placement, and develop optimal siderite dosing estimates for long-term pH control in support of remedial design for a major sediment remediation project.
Diagenesis affects carbonate $\delta^{53}$Cr: Evidence from the K-Pg boundary section at Stevns Klint (Denmark)

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The chromium isotopic composition ($\delta^{53}$Cr) of marine sediments is a valuable tool to detect changes of the redox state of paleoenvironments [1, 2]. Recently, the $\delta^{53}$Cr of marine carbonates has shown to be a very sensitive tracer of atmospheric $O_2$, weathering and hydrothermal input [3]. We applied this new tracer to the K-Pg boundary sequence at Stevns Klint (Denmark), comprising non-cemented chalk and bryozoan limestones of the uppermost Maastrichtian to lower Danian. The $\delta^{53}$Cr data was complemented with other geochemical tracers in order to explore environmental changes before and after the K-Pg extinction event.

We observe a conspicuous 3-step $\delta^{53}$Cr evolution from strongly positive values at the base of the section ($\sim +0.7\%$) to intermediate values just below the boundary layer ($\sim +0.3$) and finally to mostly negative $\delta^{53}$Cr values ($\sim -0.07$) after the K-Pg event, reflecting mantle inventory [4]. Several lines of evidence suggest that this distinct trend may not reflect a primary oceanographic signal but is the result of post-depositional alteration. A prominent diagenetic component is implied by the Sr concentration and Sr/Ca data, which match the decreasing Cr trends. Increasing Mn and Fe concentrations as well as Mg/Ca ratios further support this interpretation. In addition, the Cr shifts can be linked to lithological changes, controlled by sea-level fluctuations. Differences in primary sediment composition may thus have led to differential diagenetic alteration of the Cr signal.

We hypothesize that the isotopically most positive $\delta^{53}$Cr values, preserved in the pure chalks of the lowermost part of the section, reflect a typical marine signal. By contrast, the moderately positive to negative $\delta^{53}$Cr values of the more coarse grained limestones in the upper part of the section, reflect removal of heavy $\delta^{53}$Cr in an open-system diagenetic regime.

References:

Arsenic sequestration by fresh and aged Fe oxidation products

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The oxidation of dissolved Fe(II) by $O_2$ leads to the formation of amorphous to poorly crystalline Fe(III)-precipitates. Because of their high sorption capacity, Fe oxidation products critically affect the fate and impact of trace elements like As in soils and sediments as well as in Fe-based engineered systems for soil, sediment and water remediation or treatment.

Related to studies on As and trace metal dynamics in soils and sediments and As removal from drinking water, we perform laboratory experiments to determine how major dissolved species in near-neutral aqueous solution affect the formation, structure and aging of Fe oxidation products. In continuation of earlier work [1,2], we currently explore the effect of molar P/Fe ratio and dissolved Si and Ca on (i) the structure of fresh Fe(III)-precipitates formed by oxidation of 0.5 mM Fe(II) at pH 7.0 and their counterparts after 30 days of aging at 40°C and (ii) the uptake and solubility of co-transformed arsenate (As(V); 500 µg/L). Both phosphate and silicate interfere with Fe(III) polymerization. The strong interaction of phosphate with Fe(III) reduces As(V) uptake in fresh precipitates above a P/Fe ratio of ~0.55 in the absence and ~0.75 in the presence of Ca. The presence of Si (at molar Si/Fe ratio of 2) does not interfere with initial As(V) uptake but effectively reduces As(V) re-solubilisation during aging by inhibiting precipitate crystallisation.

The mechanistic insight gained from well-constrained laboratory experiments helps to rationalize observations from natural and technical systems, for example related to As and Fe co-sequestration at natural redox interfaces or to Fe-based drinking water treatment for As removal. The results are also relevant with respect to the sequestration of other trace elements by fresh and aged Fe oxidation products, a topic that we will address in future experiments.

References:
Dark production of reactive oxygen species in freshwaters

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Reactive oxygen species (ROS) superoxide (O2•−), hydrogen peroxide (H2O2) and hydroxyl (OH) can affect metal redox speciation and organic carbon cycling in natural waters. In this study, we focus on hydrogen peroxide, the product of superoxide reduction and the source of strong oxidants including hydroxyl, via Fenton’s reaction.

We measured production and decay rates of hydrogen peroxide in dark incubations of freshwater samples from a variety of systems. Dark production was found to be a ubiquitous feature of freshwater environments, and both production and decay rates were generally related to the concentrations of microorganisms in the samples. Production rates ranged from undetectable to greater than 200 nM hr−1, with large temporal fluctuations in two field sites that were sampled repeatedly. Filtering decreased, but did not always eliminate, production of hydrogen peroxide, indicating chemical as well as biological sources of ROS. Our results suggest that metal reactions involving ROS are likely to occur even when photochemical ROS production is minimal.

The dependence of siderophile element partitioning on Pressure, Temperature, fO2 and S-content

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The partitioning of siderophile elements between liquid metal and liquid silicate provides information about the conditions that dominated during core formation in the Earth and other terrestrial planets. In particular high pressure – high temperature experiments, performed in a multianvil apparatus, and the quantification of the partitioning behaviour in the form of partition and exchange coefficients yield conclusions about former pressure, temperature and oxygen fugacity conditions. We have chosen a broad range of elements for our experiments, namely the refractory elements Ni, Co, W and Mo, as well as the moderately volatile elements Ag, As, Au, P, Ge, Cu and Sb and the volatile elements Sn and Pb. We have investigated the partitioning behaviour over the P-T range 11-23 GPa and 2200-2800 K respectively. Oxygen fugacities of -2 to -5 log units relative to the iron-wüstite buffer have been determined, enabling us to draw additional conclusions about the valence state of the elements of interest in the silicate melt. In addition, we have investigated the effect of the S content of liquid metal on partitioning because S contents were likely significant, especially during the late stages of accretion.

The most siderophile of the studied elements, gold, exhibits the strongest temperature dependence with exchange coefficients varying over one log unit within a temperature range of 2400-2600 K. Other elements, in particular Pb, show no significant dependence on temperature. The partitioning behaviour of Pb furthermore seems to be unaffected by pressure. With 10 wt% S in the starting material, the exchange coefficient for Sn decreases by 0.5 log units, and converges with the exchange coefficient of Pb, a condition that has to be fulfilled because Pb and Sn are depleted by the same extent in the Earth’s mantle.

The results are being incorporated into an accretion/core formation model in order to understand the timing of volatile element addition to the Earth.
Serpentinization, metasomatism and carbonate precipitation in Jurassic mafic and ultramafic seafloor

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Several Ligurian ophiolitic units are considered to be fragments of heterogeneous Jurassic lithosphere that record tectono-magmatic and alteration histories similar to those documented along the Mid-Atlantic Ridge, such as at 15°20’N area and the Atlantis Massif at 30°N. We present a petrological and geochemical study of deformation and fluid-rock interaction in the Bracco-Levanto ophiolite complex (BL), which documents a multiphase history of alteration and hydrothermal activity, similar to present-day hydrothermal processes in oceanic core complexes at slow-spreading ridges. A focus is on investigating mass transfer, fluid flow paths, and fluid fluxes during high and low temperature hydrothermal activity, and on processes leading to hydrothermal carbonate precipitation and the formation of ophicalcites, which are characteristic of the BL sequences.

Bulk rock and mineral compositional data allow us to distinguish (1) a widespread phase of Si-metasomatism during progressive serpentinization, and (2) multiple phases of veining and carbonate precipitation associated with circulation of seawater and high fluid-rock ratios in the shallow, ultramafic-dominated portions of the Jurassic seafloor. In general, the ophicalcites have higher Si, Al and Fe concentrations and lower Mg than the serpentinite basement rocks with minimal or no carbonate veins. We interpret the zones of ophicalcites to reflect paleo-pathways for hydrothermal fluids and Si-metasomatism during uplift and emplacement on the seafloor. Bulk rock major and trace element data and Sr-isotope ratios indicate a seawater source of the hydrothermal fluids, and suggest that these fluids had reacted with rocks of mafic composition. We observe regional variations in Mg, Si and Al, which suggest Si-flux towards reacted with rocks of mafic composition. We observe regional variations in Mg, Si and Al, which suggest Si-flux towards Si-flux towards oceanic crust.

Serpentinization, metasomatism and carbonate precipitation in Jurassic mafic and ultramafic seafloor

Noble gas temperature determination in fluid inclusions - method, tests, future applications

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Concentrations of dissolved atmospheric noble gases in open water bodies and ground water have successfully been used to reconstruct past climatic and hydraulic conditions [1]. We have developed a combined vacuum crushing and sieving (CVCS) device which allows application of the so-called noble gas thermometer also to samples containing water amounts in the sub-milligram range, such as speleothems [2]. During growth, speleothems trap minute quantities of drip water, whose noble gas concentrations depend on the cave temperature. CVCS enables extraction of this water and the associated dissolved noble gases for analysis without inducing elemental fractionation, and minimizes addition of noble gases from air-filled inclusions. Air-related noble gases do not carry a temperature signal and have hence hampered noble gas temperature (NGT) determination in the past.

CVCS performance has been tested on samples from a stalagmite grown at a known temperature. NGTs deduced from the sieved grain size fractions with the most suitable air/water volume ratios excellently reproduce the expected paleotemperatures [2]. Furthermore, we report NGTs deduced from a stalagmite from Borneo covering two glacial–interglacial cycles (330-460 ka; [3]). These NGTs are compared to a sea surface temperature record from a tropical West Pacific sediment core [4]. We anticipate to apply the CVCS technique also to other fluid-inclusion bearing materials such as organic shells, corals, and consolidated sediments in the future.

Production and certification of Pd and Pt single spikes

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So-called spikes are solutions of isotopically enriched elements, which are used in isotope dilution mass spectrometry (IDMS) for the accurate quantification of element concentrations. Based on its proven records, especially in reference material certification IDMS is considered as one of the most powerful and most accurate methods for determining amounts of substance. [1] Contrary to other calibration approaches, IDMS does not directly suffer from long-time changes or drifts in instrument sensitivity. Moreover, provided isotopic exchange between the sample and spike is ensured, losses of analyte do not affect the analytical result. Both advantages are based on the fact that IDMS only requires isotope ratio measurements and isotope ratios are largely unaffected by instrumental drift, setup or by matrix, unless an isobaric interference is present.

IDMS often is applied for quantification of platinum group elements (PGE), either for reference material characterization or for geochemical research. [2] The main reasons for that are the required accuracy and the low PGE mass fractions in the sample. A crucial point in IDMS is, however, the availability of certified spikes. Unfortunately, no such certified spike solutions are available yet for PGE.

To fill this gap, at least partially, two single PGE spikes, one $^{106}$Pd and one $^{194}$Pt spike, have been produced and characterized. The selection of the isotopes, the production of the solutions and the ampoulation will be described in this presentation. Details on the characterization of these spike solutions by reverse IDMS using a primary assay for Pd and Pt will be given offering high purity (> 99.9). All relevant data – mass fraction of the spike isotope, isotopic composition and measurement uncertainties – will be presented. Both spike solutions are intended to become certified reference materials under the ERM® label [3].


Microbial response on siderophores of heavy metal resistant streptomycetes

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Large soil contamination by mining activities poses a severe environmental problem. The former uranium mining district Ronneburg (Thuringia, Germany) has been mined for more than 40 years until remediation of the area started in the 1990’s. Resulting from mining, the banks of the creeks in the area show high concentrations of Ni, Cu, Mn and Zn and microorganisms have to adapt to these conditions. Thus, the area represents a store to screen for heavy metal resistant strains and their resistance mechanisms, such as the excretion of chelating ligands like siderophores. These mobilise, transport and store Fe$^{3+}$ as well as other (heavy) metals in the environment. This causes a modulation of metal availability to other organisms and may influence motile and growing organisms to perform chemotaxis towards or away from a siderophore gradient to get into better living conditions.

Through the application of a new agar-plate method we were able to investigate chemotactic behaviour of different fungal and bacterial isolates to siderophores. A defined content of siderophores in culture supernatants of three different heavy metal resistant Streptomyces strains was supplied with Fe-deficient agar media in divided plates. Streptomycetes as well as fungi were inoculated on the non-siderophore containing side of the plate. Their growth was monitored with respect to effects exerted by the added siderophores.

Fungal strains showed faster growth towards the siderophore-free side while there, changes in morphology to fruitbody producing stages with increased development of aerial mycelium. Expecting a shift in the main area of growth for the whole colony, the tested Streptomyces strains displayed negative chemotaxis with siderophores while control showed equal growth. The strains S. acidiscabies E13 and S. tendae F4 showed lacks of substrate mycelium and a different pigment production indicative of a stress reaction.

Our results suggest that siderophores may play an important role in nature, not only in modulating metal availability, but also as signalling molecules.
Complex urban geochemical analysis of attic dust samples in an industrial area, Ajka, Hungary

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Recent studies suggest that airborne pollutants can be efficiently studied by the means of attic dust analysis. At Ajka region (Hungary), emissions from mining, coal-fired power plants and alumina industry have left the legacy of contamination. The major objective of this research was to study the geochemical behaviour and distribution of toxic elements in attic dust and to identify contamination source using geochemical, statistical and mineralogical methods. The sampling strategy followed a grid-based stratified random sampling design and 30 samples were collected in 27 houses within the 64 km² project area. The total concentrations of the major and toxic elements (As, Pb, Cd, Cu, Ni and Zn) were measured with ICP-OES and Hg content was analyzed with AAS. Phase analyses of the samples were carried out by the means of scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) and X-Ray diffraction (XRD) methods. Results show that the studied attic dust at the Ajka urban area was contaminated mostly by Hg, Pb and Zn with concentrations ranging between 0.1-2 mg/kg, 42.5-881 mg/kg and 90.2-954 mg/kg, respectively. The most frequently identified mineralogical phases were quartz, carbonate, gypsum and Fe- and Al-bearing phases. Based on the SEM and the ICP-OES results, the Power Plant can be considered as the most influential industrial contamination source in the studied urban area.

Halogenated anthropogenic trace gases: The atmospheric imprint and the search for new tracers

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The atmospheric burden of anthropogenic long-lived trace gases has produced powerful transient tracers of fluid motion and time-dependent processes in aquatic systems (e.g. CFCs, SF6). However, for the CFCs, the Montreal Protocol regulations have lead to reduced emissions and to atmospheric trend reversal. The resulting ambiguity in the transient signals and the eventual disappearance from the atmosphere launches a search for new tracers. Under this view we present records of atmospheric halogenated trace gases, mainly from the Advanced Global Atmospheric Gases Experiment (AGAGE). Quasi-continuous in-situ measurements of more than 50 compounds are made at several stations around the globe. The measurements track the global atmospheric background as well as signals of regional pollution such as the Asian outflow. The records are completed back in time using air archives such as air stored in canisters and polar firn. The measurements include the major ozone-depletion gases, which are regulated by the Montreal Protocol, and their replacements, most of which are powerful greenhouse gases that are regulated within the framework of the Kyoto Protocol. Chlorofluorocarbons (CFCs) have been replaced by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). These trends toward the use of less stable substances is advantageous from the climate perspective but poses difficulties when used as aquatic tracers. Perfluorocarbons (PFCs, e.g. CF4), which are extremely stable atmospheric compounds (lifetimes are 1000nds of years) are another group of potential new tracers. In addition to inertness in air and water, there are numerous additional requirements for the usefulness as tracer, such as atmospheric abundance, history and trend, solubility, and sensitivity to current measurement techniques.
The Phanerozoic $\delta^{88/86}$Sr record of seawater: New constraints on past changes in oceanic carbonate fluxes

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The isotopic composition of Phanerozoic marine sediments provides important information about changes in seawater chemistry. In particular, the established radiogenic Sr isotope system is a powerful tool for constraining plate tectonic processes and their influence on atmospheric CO$_2$ concentrations. However, the $\delta^{88/86}$Sr isotope ratio of seawater is not recording temporal changes in the marine Sr output flux, the latter controlled mainly by the burial of CaCO$_3$ on the ocean floor. Here, we present the first stable isotope record of Sr for Phanerozoic seawater ($\delta^{88/86}$Sr$_{sw}$), which we consider being sensitive to imbalances in the Sr input and output fluxes. This $\delta^{88/86}$Sr$_{sw}$ record varies from ~0.25‰ to ~0.60‰ with a mean of ~0.37‰. Overall, the Phanerozoic $\delta^{88/86}$Sr$_{sw}$ record resembles that of the Ca isotope record ($\delta^{44/40}$Ca$_{sw}$), but differs considerably from the radiogenic Sr isotope record ($\delta^{87/86}$Sr$_{sw}$). This implies different controlling mechanisms for the two Sr isotope systematics in the oceans. A new numerical modeling approach, which considers both $\delta^{88/86}$Sr$_{sw}$ and ($\delta^{87/86}$Sr$_{sw}$)$_{sw}$, yields improved estimates for Phanerozoic fluxes and concentrations for seawater Sr. During the Phanerozoic, the oceanic net carbonate flux of Sr (F(Sr)$_{carb}$) varied between an output of $-4.7 \times 10^{10}$mol/Myr and an input of $+2.3 \times 10^{10}$mol/Myr with a mean of $-1.6 \times 10^{10}$mol/Myr. On time scales in excess of 100Myrs the F(Sr)$_{carb}$ is proposed to have been controlled by the relative importance of CaCO$_3$ precipitates during the “aragonite” and “calcite” sea episodes. On time scales less than 20 Myrs F(Sr)$_{carb}$ is likely controlled by short-term variations in carbonate burial rate (linked to ocean acidification or anoxia) and changes in carbonate weathering and recrystallization on the shelf, leading to transient changes in the oceanic carbonate alkalinity budget.

High-temperature rheology of a megacryst-bearing mugearitic magma from Etna (Italy)

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We performed a series of concentric cylinder viscosity measurements at high temperature (1000 < T < 1400 °C) and high strain rates ($10^{-3}$ – $10^{1}$ s$^{-1}$) to investigate the multiphase rheology of a mugearitic lava from Etna volcano. Natural samples exhibit porphyritic index ranging between 30 and 60 vol%. The mineral assemblage is constituted by megacrystic plagioclase (20–50 vol%), phenocrysts of olivine, augitic clinopyroxenes and Fe-Ti oxides, and a microcrystalline groundmass composed prevalently of plagioclase (75 vol%). The knowledge of the rheological evolution during crystallization is paramount in order to understand completely the dynamics of magma transport from the storage zones up to the surface. We have firstly measured the viscosity of the pure liquid phase on both the bulk rock (i.e. initial crystal-free magma) and the separated groundmass (i.e. residual liquid). The slight compositional variation due to crystallization does not affect substantially the viscosity. The contribution of plagioclase megacrysts to magma rheology has been then evaluated through a set of experiments on partially re-melted samples. We defined a temperature-time window in which groundmass is completely melted and different amounts of megacrysts (20-50 vol%) are preserved. Results confirmed the dependence of rheology on the textural features (crystal content, shape, orientation and size distributions) of the crystal-liquid suspension. The characteristics of these samples allowed us to investigate the viscous flow behavior of medium-high concentrated suspensions at strain rates and temperature pertaining to the natural systems. The results of this study were compared with literature models predicting the rheological behavior of crystal-bearing suspensions and were used to constrain the history of storage and transport of these peculiar magmas.
Plagioclase crystallization kinetics in basalts by high-T viscosity measurements
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In this study we explore the effect of undercooling and stirring on the crystallization kinetics of remelted basaltic material from Stromboli (pumice from the 15th March 2007 paroxysmal eruption) and Etna (1992 lava flow). Isothermal crystallization experiments were conducted at different degrees of undercooling and different applied strain rate (T=1157-1187 °C and strain rate = 4.26 s⁻¹ for Stromboli; T=1131-1182 °C and strain rate = 0.53 s⁻¹ for Etna). Melt viscosity increased due to decreasing temperature and increasing crystal content and achieved a steady value after 10⁴-10⁵ s. The mineralogical assemblage comprises sp + plg (dominant) ± cpx with an overall crystal fraction between 0.06 and 0.27, increasing with undercooling and flow. Both degree of undercooling and deformation rate deeply affect the kinetic of the crystallization process. Plagioclase nucleation incubation time strongly decreases with increasing ΔT and flow. Plagioclase growth rates G display relative small variation with Stromboli samples (high strain rate) showing higher values (G=10⁻⁷.7 m s⁻¹) compared to G values from Etna samples (low strain rate; G=10⁻⁸.5 m s⁻¹).

G values obtained in this study are generally one or two order of magnitude higher compared to those obtained in literature for equivalent undercooling conditions. Stirring of the melt, simulating flow or convective conditions, facilitates nucleation and growth of crystals via mechanical transportation of matter, resulting in the growth rates observed. Any modeling pertaining to magma dynamics in the conduit (e.g. ascent rate) and lava flow emplacement (e.g. flow rate, 'a'a transition) should therefore take the effects of dynamic crystallization into account.

Fast hydration of volcanic glass at low temperatures
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During volcanic eruptions, magma loses most of its volatiles and cools below the glass transition temperature. However, natural volcanic glass is often oversaturated in water. The water often is distributed inhomogeneously and local increases can be observed around textural features such as bubbles, crystals and cracks. The origin of these heterogeneities can either be redistribution of magmatic water or dissolution of meteoric water. However, the processes of dissolution of water in a solid glass and in a silicate melt at elevated temperatures vary significantly and the quantities, timescales and speciation of water dissolution and diffusion remain poorly constrained.

We present preliminary results of water measurements on naturally hydrated volcanic glass and experimentally hydrated silicate glasses. Water heterogeneities in natural, volcanic rhyolitic glass around cracks, bubbles and spherulitic crystals as well as flow banding show increases of up to ~0.2 wt. % above the general water concentrations of ~0.045 to 0.1 wt. %. Textural and numerical proxies based on bulk water diffusion indicate timescales of hydration from hours to months. We propose to adapt these models to consider water speciation and variation with temperature.

To estimate timescales and quantities of hydration, we rapidly hydrated natural and synthetic (Fe-free) glass in a water vapor saturated Argon atmosphere at temperatures below the glass transition while recording enthalpy and gravimetric changes in a simultaneous thermal analysis. Preliminary data shows that a weight gain of 0.15 wt. % in hydration can be reached over 10 h at 400°C. We evaluate the possibility for glass to physically intrude nanopores and chemically diffuse into the structure. Therefore common models of water dissolution, speciation, and distribution in silicate glasses need to be revised for low temperatures and further experimental and analytical work is needed to create reliable quantitative models.

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River denudational transport to the sea using the oceans
$^{10}$Be(meteoric)/$^{9}$Be ratio

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The ratio of the meteoric cosmogenic nuclide $^{10}$Be (T$_{1/2}$ = 1.39 My) to the stable isotope $^9$Be is a proxy of terrigenous input into the oceans. The system combines a tracer of roughly constant flux to the Earth surface (over time scales characteristic of weathering) with one that depends on its release rate from rock by weathering. Using a mass balance model we previously quantified how the $^{10}$Be(meteoric)/$^9$Be ratio traces weathering and erosion from the soil to the river scale [1].

Here we take this tracer further by exploring this isotope ratio when river dissolved and sedimentary material is discharged into the ocean, where meteoric $^{10}$Be is added by direct precipitation into the oceans. Using river Be data we first find that the fraction of mobile $^9$Be (meaning unlocked from silicate minerals that is now either dissolved or adsorbed onto sedimentary particles) in rivers is globally 20%. We next find that a measured ocean dissolved $^{10}$Be/$^{9}$Be ratio of about 1x10$^{-7}$ [2] is satisfied by the mass balance if only 10% of the mobile river Be is eventually dissolved into the oceans by boundary exchange. This number is obtained using the sum of global solid and dissolved river fluxes [3], an average crustal $^9$Be concentration of 2.5ppm, and an atmospheric $^{10}$Be flux of 1x10$^{10}$ atoms g$^{-1}$cm$^{-2}$.

There is good agreement between modeled and measured ocean $^{10}$Be/$^{9}$Be ratios when we perform this mass balance for each ocean basin. Only the southern Atlantic deviates from the predicted value, which can be explained by the dominant external deep and bottom water inputs that affect the measured ratio.

We show that the fraction of mobile $^9$Be does not change significantly over a large range of global denudation rates. Therefore, the $^{10}$Be/$^9$Be ratio can serve as a tracer that, unlike radiogenic and stable isotope ratios, truly quantifies past denudation rate and hence terrigenous input into the oceans at a temporal resolution exceeding the residence time of Be in the oceans (ca. 600 years).


Quantification and speciation study of the marine solid-phase iron pool

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Iron chemistry is tightly linked to marine primary productivity, particularly in High Nutrient Low Chlorophyll (HNLC) regions of the world's oceans, where Fe is commonly the limiting nutrient. Only about one third of the total iron present in the upper 200m of the open ocean water column is present in the smallest 'soluble' size fraction; the remainder is bound to colloidal ligands or incorporated into particles and biology greater than the 0.02µm-1000kDa size cut-off. From analyses of a global dataset, colloidal Fe (cFe) behaviour is found to vary between different ocean basins and there is evidence for a seasonal cycle in cFe concentration, associated with depletion during the summer growth season. Controls on distribution and concentration of this (quantitatively more important) larger Fe size class are linked to distance from shore, ambient ligand concentration, and colloid stability and inorganic solubility.

Despite the importance of size-fractionated Fe study, complementary chemical and mineralogical information is required to more fully understand the role of solid phase Fe in the marine system. We have developed a novel Fe L-edge x-ray technique that incorporates both high-resolution (12nm resolution) scanning transmission X-ray microscopy and in-situ L$_3$-edge XANES spectroscopy. Local chemical information derived from the XANES spectra reflect variations in Fe valence state, ligand type and coordination, and the degree of distortion within Fe polyhedra. For use in mineralogical identification of sub-micron sized particles, we present a 2D graphic plot based on variations in the spectral parameters of standard Fe-rich phases. Despite some limitations associated with particle thickness and spectral saturation, this plot has been successfully applied in speciation studies of particles collected from both marine and fluvial systems. A case study is presented highlighting significant chemical differences identified in marine particles (20-700nm in diameter) sampled from the euphotic zone of the different frontal zones of the Southern Ocean. The implications of these differences are discussed in terms of particle solubility and biological availability.

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Detection of engineered cerium oxide nanoparticles in the environment

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Cerium oxide (CeO₂) nanoparticles are increasingly used in products such as diesel fuel combustion catalysts. CeO₂ nanoparticle emission into the environment is of concern due to potential ecotoxicological effects. The detection of engineered CeO₂ nanoparticles in environmental matrices poses a challenge due to predicted concentrations in the part-per-trillion range and the differentiation from nanoparticulate Ce-containing minerals occurring in nature.

Data provided by the Forum of European Geological Surveys (FOREGS) show La:Ce ratios of 0.50 ± 0.05 in bulk topsoils and stream sediments sampled across Europe, while engineered CeO₂ nanoparticles exhibit La:Ce ratios in the range of 0.001 to 0.002. Therefore, deviations from the “natural” La:Ce ratio may potentially be used for the identification of engineered CeO₂ nanoparticles in environmental matrices.

Sediment and preconcentrated water samples from uncontaminated sites were analyzed by flow field-flow fractionation (FFF) coupled to light scattering detection and inductively coupled plasma mass spectrometry (ICPMS) to determine size distributions and elemental composition of the natural nanoparticles. Preliminary results show that La:Ce ratios are constant at about 0.5 across the natural nanoparticles from unpolluted streams.

By addition of engineered CeO₂ nanoparticles at various concentrations to the natural nanoparticle suspensions followed by FFF analysis, we probe the sensitivity of the size-resolved La:Ce ratios as a tool for determination of engineered CeO₂ nanoparticles. FFF size fractions were collected and analyzed by single particle ICPMS, with the aim of differentiating between natural Ce-containing suspended particulate matter and engineered CeO₂. The results were compared to samples from potentially contaminated road runoff samples.

Preliminary findings on the strengths and weaknesses of these methods for the detection of engineered CeO₂ nanoparticles in environmental matrices will be presented.

Hydrological change in the Turkana Basin through the termination of the African Humid Period: The lacustrine Sr-isotope record

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At the Termination of the African Humid Period (AHP) important hydrological changes occurred in NE Africa. Lake Turkana in Northern Kenya is one of the larger lakes in the East African Rift Valley and its Holocene history is relatively well studied. The lake dropped by ~ 80 meters at the end of the AHP, presumably caused by a reduced water supply from the Ethiopian highlands, brought to the lake by the Omo River. The Omo River at present supplies more than 80% of the water to Lake Turkana. In the Holocene this situation was different, with significant water supplied to Turkana by two neighbouring Basins: The Chew Bahir Basin to the Northeast and the Suguta Basin to the South.

Here we have analysed the Sr isotope variation of Holocene ostracods and bivalves to identify Holocene changes in water provenance to Lake Turkana. Results show a clear trend in Holocene Sr isotope values. We interpret higher values in the Early Holocene to reflect significantly increased contribution of water from the Chew Bahir Basin. Application of a Sr-isotope mass balance model allowed us to put constraints on the magnitude and rate of hydrological change in Lake Turkana.

The combined signature of Sr- and oxygen isotope variation in Holocene Lake Turkana is in line with a previously postulated increase in rainfall sourced from the Indian Ocean in the Horn of Africa at AHP times.

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CA-U-Pb zircon dating obtained by the LA-ICP-MS system: Impact for their interpretations

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Laser ablation ICP-MS is a powerful method to determine the age of rocks by measuring U/Th/Pb isotopes. The method is fast, cheap and several applications present precise (< 1% 206Pb/238U age errors) and accurate results using corrections and reference materials [1]. For several years U-Pb zircon analyses by TIMS are using the CA [chemical abrasion] technique to avoid domains that have lost Pb parts [2,3]. In this work we apply the same CA technique for LA-ICPMS analyses, using the Excimer 193nm laser system with a constant geometry ablation cell connected to the quadrupole ICP-MS (PerkinElmer, Elan 6100). The selected target material are zircon grains of intrusive rocks with ages of 24 Ma (Miocene) and 80 Ma (Cretaceous) that show no inherited components.

The analyses we include TIMS and LA-ICPMS measurements of U/Pb ratios of CA- and non CA-treated zircons. All non CA-treated zircon measurements show a broader range of their 206Pb/238U ages including ratios which refer to recent lead loss or to small inherited Pb components. The CA-treated zircon measurements show a more homogenous age pattern due to the removal of domains with lead loss. In the case of not overlapping concordant ages the cluster with the youngest ages should be interpreted as time of magma crystallization, which is an important advantage of the techniques. Most publications [4] take the 2 sigma error into account for their calculation of 206Pb/238U ages; following this procedure we can demonstrate that the non CA-treated U/Pb ages are not overlapping with the CA-treated zircon grains measured by LA-ICP-MS and TIMS techniques. The standard error of this mean has even less geological significance if age variations are real [5]; note that the value of the standard error of the mean would decrease if greater numbers of zircons were measured.


Souring control by six years of nitrate injection into a low temperature oil field

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Production of oil by water injection can result in souring by sulfate-reducing bacteria (SRB). Souring can be prevented or reversed by inclusion of nitrate in the injection water, which boosts the activity of nitrate-reducing bacteria (NRB). In the Medicine Hat Glauconitic C (MHGC) field, oil production through water injection was started in 2000. Souring, was noted in 2006. Field-wide injection of 2 mM nitrate was adopted as a souring control strategy in 2007. We have monitored the success of this strategy by monthly sampling of producing wells and analyzing the concentrations of sulfate, sulfide, nitrate and nitrite [1], as well as by determining microbial community composition [2].

Field-wide nitrate injection decreased produced sulfide initially, but this was followed by recovery. Microbial zonation in which NRB grow close to the injection wellbore and SRB deeper in the reservoir was the suggested cause for this. Successful injection of nitrate pulses exceeding the nitrate reduction capacity of the NRB gave credit to this idea [1]. Constant nitrate injection over the past 6 years has given nitrate breakthrough at an increasing number of injection wells. This was associated with removal of sulfide, as well as with breakthrough of sulfate, nitrate and nitrite. Production of oil/water depleted of toluene and other alkylbenzenes and containing increased proportions of the toluene-utilizing NRB Thauera were also observed [2].

Long-term injection of nitrate and changes in water management strategy have caused a near complete reversal of souring in the MHGC field. Despite lack of success in the first two years persistence has since paid off.

Geochemistry of uranium in the reduced carbonaceous sediments of small lakes in Baikal Region

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The most commonly identified pathway to explain the accumulation of authigenic U in reduced sediments is the microbially mediated reduction of U(VI) to less soluble U(IV) [2]. However previous researchers could not acquire the direct evidence of uranium reduction and formation of its poorly soluble oxides, so the additional investigation of the problem is needed [1]. Our work is aimed at detecting of U reduction process in sediments of two small lakes (fresh and salt) which are located in the Baikal region. To achieve this goal we separated sediments to lithogenic and various authigenic fractions using the method of sequential extraction, which is based on the method of Tessier [3]. According to our research values of activity ratios (²³⁴U/²³⁸U) in the insoluble residue significantly differ from 1 in both lakes. This indicates the presence in the residuals not only the lithogenic fraction, but a noticeable amount of UO₂. Uranium accumulates in lake sediments mainly through chemogenic processes, in different forms (in oxides and hydroxides, organic matter or isomorphic impurities in carbonates). This work was supported by grant RFBR 12-05-31087mol_a


Volatilization of methylated selenium, sulfur and arsenic from a wetland

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Selenium (Se) is an essential trace element for life. However, it can negatively affect human health due to its narrow range of beneficiary concentration and its unequal distribution in the surface environment. To date, sources, sinks and fluxes in the global Se cycle are poorly understood and quantified. Although methylation and volatilization of Se from terrestrial environments is known to occur (and is studied for e.g. bioremediation purposes), its relevance to the natural global atmospheric Se budget remains unknown.

We applied a novel chemotrapping method in combination with a flow-through chamber system to identify and quantify volatilization of Se, sulfur (S) and arsenic (As) from a minerotrophic peat bog in southern Switzerland. We were able to determine gaseous fluxes of Se (0.11 µg Se.m⁻².d⁻¹), S (37 µg S.m⁻².d⁻¹) and As (0.16 µg As.m⁻².d⁻¹) in the form of non-, mono- and di-methylated species. By comparing these fluxes with total concentrations of these elements in both the peat and surface water, it became evident that Se is approximately 40 to 110 times more efficiently volatilized from the peat bog than As and S, respectively. Furthermore, we observed that elevated temperatures increased volatilization of the investigated elements to a different extent. Our results suggest that Se volatilization from wetlands, and possibly other terrestrial environments, may crucially influence the biogeochemical cycle of Se.

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Early Paleozoic intrusives of the Kuznetsk Alatau, Siberia: Isotopic evidence of oceanic lithosphere participation in sources

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Products of the Early Paleozoic intrusive magmatism are represented in the Kuznetsk Alatau (KA) by granitoid, gabbro-syenite, and alkali basite complexes. They were formed during the period of about 510-490 Ma, which is in the Central Asian fold belt [1]. The magmatic activity implies the presence of multi-component melt sources with age that close to the age of the oceanic lithosphere formation. Nd-Sr isotopic signatures discovered for four studied complexes formed in different ways indicate possible participation of Paleo-Asian Ocean (PAO) lithosphere in the processes of magma generation at the Early Paleozoic stage of this ocean’s evolution. The oldest complexes (about 510 Ma) are the differentiated series from gabbro to granodiorite as well as alkaline basic complexes. Despite the petrogenetic differences, these complexes have similar isotopic composition of Nd (εNd ~ +4.8…+5.0). Such values are typical either for magmatic derivatives of moderately depleted mantle, or for mixing products of DMM or PREMA reservoirs with EM-type mantle and continental crust materials. The influence of crust contamination is seen in high ratio of Sr-isotopes in the rocks (εSr ~ +1…+28). Granitoids and gabbro-syenite series with the age of about 500-490 Ma don’t have significantly different Nd-isotopic compositions (εNd ~ +3.5…+4.6). Apparently, it is confirmed by narrow range of these εNd(147) values (~ 0.8–0.9 Ga). According to different views [2, 3], the beginning of the Rodinia supercontinent’s break-up, and following the PAO opening are estimated to be 970–800 Ma Based on our data, Sm-Nd isotopic age of ultrabasites and gabbroids of the layered series and restite suites varies from 955 to 890 Ma, respectively. Magmatism probably developed under the conditions of plume interacting with active continental margin coupled with MORB+PREMA+EM matter mixing.


Mineralogical and geochemical variations in lower Godavari River sediments, Peninsular India: Implications to source rock weathering

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Godavari River is the third largest river in the Indian sub-continent, which originates in the Deccan Traps and drains an area of 3.1 x 105 km2. The river flows in the east and the south-easterly direction for a distance of 1465 km before discharging into the Bay of Bengal. The major, trace and rare earth elements geochemistry and clay mineral compositions in bed sediments from lower reaches of Godavari River suggest that they are derived from weathering of felsic rocks. Trace and rare earth elemental compositions indicate evidence of sedimentary sorting during transportation and deposition. Lower concentrations of transition elements, such as V, Ni and Cr imply enrichment of felsic minerals in these bed sediments. The REE pattern in lower Godavari sediments is influenced by the degree of source rock weathering. The light rare earth elements (LREE) content are indicating greater fractionation compared to the heavy rare earth elements (HREE). A striking relationship is observed between TiO2 and ΣREE content suggesting a strong control by LREE-enriched titaniferous minerals on REE chemistry. Shale-normalized REE pattern demonstrate a positive Eu anomaly, suggesting weathering of feldspar and their secondary products, which are enriched in Eu. Chondrite-normalised REE pattern is characteristic of felsic volcanic, granites and gneissic source rocks. Trace elemental compositions in sediments located near urban areas suggest influence of anthropogenic contamination. Chemical Index of Alteration (CIA) is high (avg. 65.76), suggesting a moderate chemical weathering environment. X-ray diffraction analysis in clay fraction shows predominance of clay minerals that are formed because of the chemical weathering of felsic rocks.

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CO$_2$ speciation and transport properties of CO$_2$-bearing silicate melts from First-Principle simulations

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There are growing evidences of the existence of CO$_2$-rich magmas in the upper mantle [1-3]. So the role of carbon-rich melts at depth is now becoming a credible scenario to explain the extraction of CO$_2$ from the source region to the surface. During the last three decades many studies have been devoted to measure the solubility of CO$_2$ in silicate melts of various composition. But due to experimental difficulties these studies were generally restricted to low and moderate pressures (below ~20 kbar). IR spectroscopy has emphasized the importance of CO$_2$ speciation which may exist either as molecular CO$_2$ or as carbonate ion (CO$_3$$^{2-}$), the molecular form being favored in polymerized (silicic) melts while the carbonate ion is dominant in depolymerized (basic and ultrabasic) melts. However it has been suggested recently [4,5] that the CO$_2$ speciation observed in quenched glasses by IR spectroscopy may not be representative of that in silicate melts equilibrated at high temperature.

To address this issue we have performed First-Principle Molecular Dynamics of CO$_2$-saturated basaltic and kimberlitic melts. The molecular form is indeed favored in the more polymerized melt. Furthermore, a new transient species is also identified. The electrical conductivity of the CO$_2$-saturated basaltic and kimberlitic melts has also been evaluated and found in good agreement with experiment. These results have also been used to develop an empirical force field for describing CO$_2$-rich melts by classical MD simulations.


Microstructural control on trace element diffusion in pyrrhotite from komatiite hosted massive Ni sulphides, Yilgarn Craton

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Pyrrhotites (Fe$_{7}$S$_{8}$) from three different komatiite hosted massive nickel sulphide deposits have been analysed with electron backscatter diffraction analysis (EBSD) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in order to understand how trace elements behave during deformation.

EBSD data reveals strain localisation microstructures in sample from greenschist facies whereas in sample from mid-amphibolite facies, pyrrhotite contains multiple parallel low angle boundaries and crystallographic preferred orientation. A sample from the upper amphibolite facies, is characterised by very large >2cm grains that contains numerous deformation twins. Laser ablation ICP-MS data reveal increased concentrations of Pb, Bi and Ag along low angle subgrain boundaries and twin boundaries. The increased concentrations of Pb, Bi and Ag are explained by diffusion of the trace elements along fast diffusion pathways (low angle and twin boundaries). Trace element variations are developed at the low-temperature stage of the tectonic history of the three deposits. Diffusion of Pb, Bi and Ag is triggered by their low solubility in sulphide phase, pyrrhotite.