Role of Hydrogen and Oxygen fugacity in incorporation of Nitrogen in reduced magmas of the early Earth’s mantle

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In a series of experiments in the system Fe-bearing melt + molten Fe phase + N + H conducted at 4 GPa, 1550 °C, and fO2 from 2 to 4 log units below IW buffer we have characterized the nature and quantified the abundance of N and H species dissolved in a model silicate melt (FeO + Na2O + Al2O3 + SiO2). To elucidate the mechanisms of nitrogen and hydrogen dissolution in magmas, we studied the glasses produced by quenching the melts using infrared and Raman spectroscopy’s in a manner similar to that reported by [1]. Experiments indicate that under the reduced conditions corresponding to the fO2 path during metal segregation and self-oxidized of mantle [2] and magma ocean [e.g. 3, 4] the silicate melt would contain species with N–H bonds (NH3, NH4+, NH2–, NH2+) as well as N2 and oxidized H species (OH– and H2O). Some hydrogen is present in the melt in molecular form. The formation of N–H bonds in the reduced silicate melts results in a significant increase in nitrogen solubility that can reach 1–2 wt. %. It is suggested that significant amounts of nitrogen, comparable to those estimated for the present-day mantle, could have been incorporated in the early Earth by dissolution in reduced magma ocean.

Support: Prog. No 24 RAS, RFBR grant No 11-05-00926, ESD RAS project No 8.

Differentiation of ophiolitic and nonophiolitic gabbros using confocal Raman spectroscopy: Central Anatolia Turkey

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Ophiolitic gabbros are mostly exposed at west of Tuz Lake and nonophiolitic gabbros are exposed at east of Tuz Lake in Central Anatolia. Ophiolitic and nonophiolitic gabbros have almost same mineral and geochemical compositions. Discrimination of the ophiolitic and nonophiolitic gabbros was carried out using the Raman spectra of the pyroxene minerals. Based on Raman peak positions, the major-element composition of the (Mg, Fe, Ca)-pyroxenes are determined and classified.

Results and Discussion

Raman vibrational modes were observed for the pyroxenes in the wave number range between 200 and 1200 cm–1 (Figure 1). The Raman modes showing the greatest variation in frequency with the Fe2+ and OH+ content are potentially capable of being used as an index for determining the ophiolite and nonophiolite pyroxenes of the gabbro series. The best Raman modes for this purpose in the ophiolite pyx series are v3 (232–540 cm–1) and (677–1046 cm–1) pairs that show about 60 cm–1 across the series. The v3 (931–950 cm–1) mode can also serve as a supplementary mode for the determination of the composition. These modes are characteristic and fairly intense. However, in the nonophiolite pyx series, because only the v3 (931–950 cm–1) and v5 (681–1046 cm–1) pairs show a variation more than 20 cm–1. These provide a weaker basis for the composition indices. The uncertainties in the determination of the Fe content with the Raman modes are of the order of 3 and 7%.

Polyphase serpentinization history of Mariana forearc mantle: Observations on ultramafic clasts from ODP Leg 195, Site 1200

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In the forearc of the Mariana subduction zone system, abundant seamounts form from extrusion of blueschist and serpentine mud. ODP Leg 195 drilled the South Chamorro seamount, where ultramafic clasts occur within the mud matrix. These clasts show a complex serpentinization history, which bears the potential for tracking the fluid history during uplift and cooling of mantle wedge rocks to the seafloor.

Highly serpentinized harzburgites, which are crosscut by different generations of late-stage veins, were examined. Preserved primary minerals include olivine (X_Mg = 0.91-0.92) and orthopyroxene (X_Mg = 0.92-0.95). Magnesium-rich (X_Mg = 0.92-0.95) clinopyroxene is present as exsolution lamellae in orthopyroxene and in symplectitic intergrowths with spinel (X_Cr = 0.48-0.59).

Multiple serpentinization steps are documented: (I) Pervasive serpentinization led to ubiquitous breakdown of olivine and formation of serpentine (X_Mg = 0.92-0.94) and magnetite. Orthopyroxene was replaced to lesser extent by serpentine (X_Mg ~ 0.90). Clinopyroxene remained stable during this stage. (II) The second hydration stage was bound to fractures crosscutting earlier serpentinization textures and is manifested as veins consisting of Mg-rich serpentine (X_Mg ~ 0.90-0.93). (III) Veins from stage II were re-activated and overprinted by serpentine + brucite assemblages. Replacement of magnetite is observed, leading to brucite with X_Mg ~ 0.80 and serpentine with X_Mg < 0.90. Furthermore, clinopyroxene breaks down and Fe-rich brucite (X_Mg ~ 0.60) forms. (IV) Finally, late discontinuous serpentine veins formed perpendicular to the stage II and III veins.

Pervasive serpentinization (stage I) likely marks a comparatively high-T (i.e. T ~ 250-350°C) hydration that took place within the mantle wedge. The lower density of the hydrated rocks led to diapiric rise and associated fracture-bound serpentine formation (stage II). Formation of Fe-rich brucite as well as breakdown of magnetite and clinopyroxene (stage III) occurred after considerable cooling (T << 200°C) during uplift. Petrography and mineral chemistry point to low-temperature demagnetization, which is in agreement with density-susceptibility relations and results of reaction-path modelling.

Incomplete recovery of mineral-bound lignin phenols

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Intimate associations with minerals is one mechanism involved in the accumulation and stabilisation of organic matter (OM) in soils. Phenolic compounds derived from partial degradation of polyphenols such as lignin are among the most surface-reactive organic compounds. However, we still do not know to which extent lignin-derived phenols associated with soil minerals can be analytically assessed.

Here, we tested the extractability of mineral-bound lignin-derived phenols by alkaline CuO oxidation.

We used tree aqueous litter (blue oak, pine, annual grass) leachates and five minerals (ferrihydrite, goethite, kaolinite, illite, montmorillonite). In a first step, we determined the sorption capacity for dissolved organic carbon for each mineral, as well as the changes in specific UV absorption during the sorptive interaction between organic matter and minerals. Then, we produced organic–mineral associations under conditions well below the sorption maximum of the contained mineral. The mineral–organic associations, the dried out leachates and the equilibrium solutions were then subjected to CuO oxidation. The amount of sorbed and not CuO-extractable lignin-derived phenols were calculated by difference.

CuO-oxidation extracted lignin-derived phenols bound to ferrihydrite completely and without changes in composition, presumably due to complete dissolution of the mineral. For all other minerals, up to 44% of the bound phenols could not be extracted. The incomplete recovery of sorbed phenolic compounds was accompanied by different ratios of extracted individual phenols, suggesting different bonding strengths.

The results show that a substantial portion of lignin-derived phenols binds irreversibly to minerals, even escaping harsh extraction unless the mineral is completely dissolved. The difference in extractability of individual phenols suggests that abiotic processes, such as sorption/desorption, should be taken into account when using CuO oxidation data for assessing organic matter transformation in mineral matrices.

Mineralogical Magazine  www.minersoc.org
Different paths of chemical alteration during grusification of granites from S Poland

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Four types of grusified granites were taken under consideration. Three of the investigated gruses were developed on the Variscan granites from Karkonosze Mts. (Kowary Średnie [KS] and Głębok [GL]) and Tatra Mts. (Skrajna Turnia Mt. [ST]), one on the Early Paleozoic (ca. 500 Ma) Izera Granite (Siedlce [SI]).

Each of studied gruses shows significant variation in the LOI (loss of ignition) value, what can be connected with degree of alteration of parent granite. Changes in contents of major elements differ for each grus localization. ST grus shows significant changes of amount of major elements in relation to degree of alteration of rock (decreasing trends in SiO2, Na2O, and CaO, and increasing trends in Al2O3, K2O, MgO and Fe2O3 contents versus LOI); SI grus shows increasing trend for Fe2O3 and MgO and decreasing trend for SiO2 (vs. LOI); in KS grus increasing trends occur for Fe2O3 and MgO, and decreasing trends for Na2O and CaO, whereas SiO2, Al2O3 and K2O content variation is non-systematic in relation to LOI. In GL grus the only slightly increasing content of Fe2O3 is visible (vs. LOI).

Using several indices of alteration [1, 2] we were able to notice differences in the paths of chemical alteration during grusification. Because the main alteration process during grusification is connected with decomposition of plagioclase, chemical alterations can be observed on plots based on changes of alkali and Al2O3 content (e.g. CIA and PIA; [1, 2]). CIA and PIA plots for ST are steeper, for SI more flattened, and for KS and GL trends are less uniform (vs. LOI). The WPI [3], which use all major elements, shows most uniform plots for each of the investigated gruses, but PI [3] shows trends only for Tatra and Izera granites, what indicate, that silica was immobile during grusification of Karkonosze granite.

The Alteration Box Plot [4] used for hydrothermal and diagenetic alteration of rocks reveals sericitization and chloritization trends in ST, KS and GL and carbonatization trend in SI.

Fluid-fluid phase separation under metamorphic conditions: MD simulations of a generalized composition H2O-CO2-NaCl

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Water and carbon dioxide are two most abundant volatile species in the Earth’s crust and mantle. They represent the common solvents which, under high-temperature, high-pressure thermodynamic conditions, dissolve various amounts of other volatiles to form complex hydrothermal and metamorphic fluids. Thus, aqueous mixtures in the system H2O-CO2-NaCl can be considered a good approximation for most crustal and mantle fluids. Although there are many experimental thermodynamic data for this generalized system, the molecular-level understanding of their thermodynamic, transport, and phase equilibria properties is still inadequate in many respects. We performed molecular dynamics (MD) computer simulations of the H2O-CO2-NaCl fluids along three high-density isochores (1.0, 1.1, and 1.2 g/cm3) to systematically study their thermodynamic, structural, and transport properties in the range of temperatures from 400 to 1000°C and pressures from 3 to 18 kbar.

The composition of H2O/CO2/NaCl = 60/28/12 mol% was chosen to probe both homogeneous and heterogeneous regions of the phase diagram. It has been predicted from experimental data [1-3] and model calculations [4-5] that such fluid would undergo phase separation at approximately 700°C by forming a CO2-rich phase of low-salinity (H2O/CO2/NaCl ~ 50/48/2 mol%) and a concentrated brine (H2O/CO2/NaCl ~ 66/20/14 mol%). We try to uncover the molecular-level mechanisms driving this heterogenization process and to rationalize the properties of decompressing H2O-CO2-NaCl fluids under metamorphic conditions in terms of the effects of temperature and density on the molecular clustering and ion pairing in the system controlled by the electrostatic and hydrogen-bonding interactions among the fluid species.

Hydrogen bonding and molecular ordering of water at mineral-solution interfaces

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Aqueous interfaces play crucial roles in many geochemical systems, and the atomic scale details of the mineral substrate structure and composition are essential to understanding and predicting their chemical and physical properties. Here we compare the results of molecular dynamics (MD) simulations for the atomic density profiles, atomic surface density distributions, hydrogen bonding configurations, and orientational ordering of H2O molecules at interfaces with several minerals, which may be considered typical for many hydrophobic and hydrophilic inorganic oxide and hydroxide surfaces [1, 2]. The atomic density profiles of water show substantial layering at all surfaces, with the details significantly different and strongly dependent on the composition and crystal structure of the mineral substrate. Relative to bulk water, the average density of water at the hydrophobic talc (001) surface is reduced by about 9-15% within 6-10 Å from the interface, which is equivalent to a 0.8Å-thick depletion layer compared to the similar but hydrophilic (001) surface of muscovite.

At the hydroxide surfaces, both cations and anions are effectively stabilized in their adsorbed state via the development of an integrated hydrogen-bonding network among the ions, H2O molecules, and surface OH-groups, even if the substrate does not charged. For organic anions, such as amino acids, the deprotonated carboxylate groups are the primary strong H-bond acceptors, whereas the deprotonated amine groups serve as only weak additional H-bond acceptors from the surface. The organic species preferably accept H-bonds from H2O molecules rather than from surface OH-groups due to structural restrictions on the development of tetrahedrally coordinated H-bonding environments for the carboxylate groups at the surface.


Paleoproductivity controls on microbial abundance in marine subsurface sediments

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IODP Expeditions 320 and 321 (Paleocene-Eocene Age Transect, PEAT) recovered a continuous Cenozoic record of the equatorial Pacific by drilling at the paleopositions of the Equator at successive crustal ages on the Pacific plate. The drilled sites passed the high productivity area of the equatorial upwelling at different times.

Microbial cell abundance in several PEAT cores strongly deviates from the expected steady decrease with depth. We compared cell count profiles with several sedimentological, physical and geochemical parameters. Several of the observed excursions in cell abundance correlate with distinct sedimentological and geochemical horizons, which are ultimately caused by changes in paleoproductivity.

Colour changes in the sediment indicate changes in redox conditions from more oxidized to reducing, they also mark the time intervals during which the site was in the high productivity zone of the equatorial upwelling. Also, distinct turning points in the cell count profiles correlate well with redox fronts, being indicated by peaks in dissolved porewater constituents like Fe²⁺ and Mn²⁺.

The new PEAT data allow an insight into how past changes in productivity are influencing current patterns of microbial abundance and activity.
Revised ages of angrites

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Angrites are a small group of 18 differentiated achondrites and are among the oldest known rocks of our Solar System. These meteorites have low metamorphism and shock effects, are enriched in refractory elements and are well suited as anchors for short-lived nuclide chronology. Therefore it is crucial to accurately measure their ages according to the Pb-Pb chronometer, the only absolute geochronometer with sufficient precision to resolve age differences in the early Solar System processes.

To determine accurate 207Pb-206Pb ages, the isotopic ratio of 238U/235U must be known. This number was assumed to be invariant at 137.88 for several decades but recent studies [1, 2] have shown that variations occur not only in terrestrial rocks but also in meteorites. In this study, we analysed six bulk angrite samples: three quenched angrites and three plutonic angrites, for their uranium isotopic ratios using the double-spike MC-ICPMS procedure after [3]. The ratios are reported relative to the recently published value of 137.837 ± 0.015 (2σ) for the uranium isotopic standard CRM145 [4]. The 238U/235U ratios for the analysed angrites are uniform within error of each other, ranging from 137.763-137.802. Analytical errors are 0.018-0.049 (2σ), depending on the sample size. These data, combined with 206Pb-207Pb analysis by TIMS, are used to revise previously reported Pb-Pb ages to values with a higher accuracy, leading to a more reliable early Solar System chronometer.

The causes of variations in the 238U/235U ratios in meteorites are currently debated, including the possible decay of extinct 247Cm to 235U. Th and Nd are used as present day proxies for the extinct Cm. Therefore, the correlation between Th/U or Nd/U and uranium isotopic ratios is used to find evidence for the decay of 247Cm in the early stages of the Solar System [1, 2]. In addition to 238U/235U values, we analysed the rare earth element (REE) pattern and the U and Th concentrations of the samples to determine the environment in which the meteorites formed and the plausibility for Cm being present during angrite formation.


Mineralogy of atmospheric particles deposited on cypress leaves close to a nuclear plant

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Enhanced activity of actinides and some decay products has been reported for the leaves of cypress trees (Chamaecyparis nootkatensis) at the edge of the Malvési uranium-processing facility, SW France. The enhanced activity is due to the release of actinides via the smokestacks and artificial ponds inside the facility. This study was conducted to characterize the particulate matter deposited on the leaf surfaces from the atmosphere and to investigate whether or not radioactive particles may be identified.

Air-dried leaf samples were examined by scanning electron microscopy (SEM), in combination with energy-dispersive X-ray spectrometry (EDX). The samples were scanned systematically in both secondary and backscattered electron modes. EDX spectra were collected from particles and from areas devoid of particles (background spectra). These background spectra as well as the signals resulting from the C or Au coating were taken into account for the interpretation of the qualitative EDX spectra of the individual particles trapped on the leaf surface.

Particles ranging in size from <200 nm to ~40 µm were found on most portions of the adaxial leaf surface, but they are especially abundant at the boundary between facial and lateral leaves. We classified the particles chemically according to the following five principal classes: carbonates, silicates, sulfates, oxides/hydroxides, and halides. Approximately 80% of all analyzed particles could be attributed to these five classes. In addition, other types of particles were found, including Fe alloys; scheelite-group phases; phosphates; sulfides; and fly ash spheres.

Of special interest are U-rich particles, which were identified as U oxides, except for one particle, which was an U-oxide-fluoride. Clearly, these particles were released into the atmosphere by the nuclear facility prior to their deposition on the leaf surfaces. As most of the U-rich particles are ≤1 µm across, they are respirable.

Once inhaled, particles containing alpha-emitting isotopes represent a potentially long-term source of ionizing radiation inside the lungs and thus, pose a threat to the health of the people living nearby.
Petrogenetic implications of two contrasting granite types in the Çataldag Plutonic Complex, NW Turkey

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In late Oligocene and Early Miocene time, western Turkey was the site of extensive magmatic activity that produced voluminous plutonic associations. This magmatic activity was followed by the continental collision between the Sakarya continent and Tauride-Anatolide carbonate platform along the Izmir-Ankara-Erzincan suture zone prior to middle Eocene. The Çataldag plutonic complex (CPC), one of the biggest plutonic associations, is a composite intrusive body consisting of both I- and S type granitic intrusions of similar age. 

39Ar/40Ar dating obtained from CPC yields ages between 20 and 22 Ma as their cooling ages. These two intrusive groups display different textural, structural and also geochemical features. S-type, peraluminous granitic intrusion in CPC is represented by synkinematic, sheet like bodies situated in the eastern border of the plutonic complex. It includes leucocratic two-mica granites and milonitic granites which show petrographical features indicating ductile shear zone deformation. They are composed of quartz, feldspar with minor biotite, muscovite, epidote and garnet. Combined petrographical and geochemical features of this group reveal crustal origin for their genesis. I type granitic intrusion is made up of granite and granodiorite- quartz diorite showing gradational contact to each other. This group is late kinematic weakly deformed intrusion and displays hipidiomorphic granular and porphyric textures. Geochemically, it has medium to high-K calc-alkaline and metaluminous compositions. Major and trace element compositions, and Sr-Nd-Pb isotope data indicate collectively that the I type granitic group of CPC has been originated from hybrid magma (s) including mantle and crustal components. Geochronological and petrological findings combined with bimodal character of CPC suggest that CPC is synextensional and therefore there was a close spatial and temporal relations between magmatism and extensional tectonics during the late Cenozoic geodynamic evolution of Turkey.

A combined U/Pb and Hf-isotope study of up to 4.0 Ga detrital zircon from the Wyoming Province

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An extensive dataset (n=750) of new zircon U-Pb dates is presented for two quartz-rich metasediments from the eastern Beartooth Mountains, northern Wyoming craton, Montana. Both rocks yielded detrital zircon dates with comparable age populations, ranging from just under 4.0 Ga to the likely deposition age of ca. 3.0 Ga. Among the Meso-, Paleo-, and Eoarchean zircon there are age groupings. The most prominent population occurs between 3200 and 3325 Ma, followed by less abundant groupings at 3500, 3625, 3725, 3850 and 3950 Ma. A representative selection of grains (n=50) were subsequently analysed for Hf-isotopes by in situ MC-ICP-MS. Of these, 44 grains define a clear linear array in a Hf-isotope evolution diagram. The oldest zircon have chondritic initial Hf-isotope composition, with all younger grains defining a clear trend towards less radiogenic compositions. At 3.25 Ga, this trend averages -12 EHz.

Whereas no rocks of Eoarchean age have yet been found in the Wyoming craton, Pb-isotope signatures of 2.8 Ga granodiorites have long been known to require involvement of an ancient high U/Pb silicate source. This could have been subduction zone modified mantle or a cratonic substrate. We discovered inherited Mesoarchean zircon in the 2.8 Ga granodiorites and heterogenous Hf-isotopes in zircon from one granodiorite, collectively favoring the in situ existence of a cratonic nucleus from the Hadean/Archean boundary but with no isotopic evidence for involvement of even older crust.

In agreement with most other Eoarchean and Hadean detrital zircon occurrences, it appears that the oldest zircon-bearing lithologies of the Wyoming craton became part of the erosional cycle only after a very extensive (ca. 1 Ga) period of residence in the crust. The internal structures of the oldest studied zircon grains reveal repeated reworking, testifying to a long and complex thermal history of the crust. This is consistent with a model of an originally quite zircon-poor mafic crust, whose internal heat, generated by radioactive decay, led to episodic remelting and reworking into a more evolved upper crust in which zircon became more abundant and a more refractory, depleted lower crust.
Vakuties in the kimberlite melt – What drives ascent and causes explosive eruption?

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Existing reconstructions of the kimberlite melt emphasise carbonate-bearing ultramafic compositions with significant amounts of dissolved volatiles CO₂ and H₂O (10-20 wt%). These volatiles are considered to be a major factor in reducing viscosity of the kimberlite melt, governing fast ascent from mantle depths. The exsolution of these volatiles from the melt during ascent and emplacement is viewed as being responsible for violent eruption of the magma and related brecciation of country rocks and the kimberlite itself. Magmatic volatiles and groundwaters have an unequivocal role in present models of kimberlite emplacement (fluidisation and phreatomagmatism, respectively).

Studies of the diamondiferous Udachnaya-East pipe (Siberia) kimberlites [1-3] show that neither of major magmatic volatiles in the form of degassing fluids was responsible for well-known 'explosivity' of kimberlites. Exceptionally fresh kimberlites from the Udachnaya-East pipe have low H₂O (<0.5 wt%), but high CO₂ (up to 14 wt%), Cl and alkalis. The carbonatite-chloride composition of the Udachnaya-East kimberlite [1, 2] and similar compositions in olivine-hosted melt inclusions in other kimberlites worldwide [4] strongly support the previously assumed low viscosity and density of kimberlite magmas. Massive degassing of H₂O and CO₂ is unlikely in the case of the Udachnaya-East kimberlite, because the melt is poor in H₂O, whereas CO₂ is bonded in the carbonatitic melt. After crystallisation of olivine the kimberlite melt evolves towards essentially dry carbonate-chloride compositions [3]. The gravitational separation of silicate solids within the kimberlite pipes drives light, low viscosity carbonate-chloride melt to the top. The hydrogen species, such as H₂ and CH₄, some of magmatic origin, but mostly produced by post-magmatic serpentinisation of olivine in the kimberlite, are the main cause of explosions. Detonation of these gases at near-surface levels of the pipe can result in brecciation and even evacuation of already solid kimberlite and country rocks.


Real composition of the Earth’s lower mantle

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Real composition of the Earth’s lower mantle is based on a study of mineral inclusions in lower-mantle diamond from Brazil, Guinea, Canada and Australia. Three associations were established among them: juvenile ultramafic, analogues to eclogitic, and carbonatitic. The juvenile ultramafic association strongly predominates; it is composed of ferropericlase, MgSi₂-, CaSi₂- and CaTi-perovskites, stishovite, tetragonal almandine-pyrope phase (TAPP), and some others. The mineralogical composition of the lower mantle is now understood to be more complex than had been suggested in theoretic and experimental works. The frequencies of the lower mantle minerals for all areas are similar to each other, deviating from the average by only 10-15 %.

These figures differ drastically from the composition of the lower mantle as suggested from experimental data. In that the most common mineral is ferropericlase, which comprises 48.0-63.3 % (average 55.4 %) of all minerals in the lower mantle. This is in contrast to an abundance of ~ 18 % as suggested by experimental data, i.e. approximately three times higher. In contrast to ferropericlase, MgSi₂-perovskite comprises, in all studied regions, only 5.0-10.2 % (average 7.5 %), i.e. approximately ten times lower than has been suggested as an average composition in the lower mantle (~ 77 %); and its composition is more iron-rich (mg = 0.36-0.90) as compared to experimental and theoretical data. CaSi₂-perovskite, according to geological data, is more than twice as common compared to experimental data (10.0-14.3 % with an average of 12.0 % against ~ 5 %). The most important feature of the real composition of the lower mantle is a permanent presence, in all regions and areas, of free silica (as stishovite), in the lower mantle. Stishovite frequency, among the lower mantle minerals, is 2.1-15.0 % (average 8.4 %). The other minerals (CaTi-perovskite, TAPP, a phase with the composition of that of olivine, spinel, ilmenites, titanite, native nickel and iron, magnetite, and sulphides), have frequencies 0.1-4.3 % each. These discrepancies suggest that the composition of the lower mantle differs to that of the upper-mantle, and experiments based solely on ’pyrolitic’ compositions are not, therefore, applicable to the lower mantle. These data indicate a probability of an alternative to the CI-chondrite model of the Earth’s formation, for example, an enstatite-chondrite model.
Short-term CO$_2$-fluid-mineral interactions in a CO$_2$ injection experiment, Wyoming

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During geological CO$_2$ storage short-term geochemical processes will be dominated by dissolution of CO$_2$ into the formation fluid and by the reaction of this acidic fluid with soluble minerals (e.g. carbonate, oxide, sulphide and organics) in the reservoir. Modelling the progress of the fluid-mineral reactions is frustrated by uncertainties in the absolute mineral surface reaction rates [1] and the significance, in natural systems, of CO$_2$ dissolution and transport in formation fluid as an overall rate limiting step.

We present preliminary results of water chemistry from an artificial noble gas tracer study in a commercial CO$_2$-EOR reservoir located in Wyoming, USA. In this study a noble gas spike ($^{3}$He & $^{129}$X) was introduced to a single CO$_2$ injection well [2], and fluids and gases collected from the surrounding four-point production well pattern, from September 2010 to February 2011. Preliminary results from fluid chemistry measured over this period reflect: (1) mobilization and mixing of formation water, driven by the injection of CO$_2$; (2) the arrival of co-injected water and CO$_2$ at the production wells and (3) dissolution of the CO$_2$ and subsequent reaction of this acidified fluid with soluble minerals in the reservoir. The spatial changes in fluid chemistry are consistent with the reservoir geology; the updip producers are dominated by processes related to the early arrival of the CO$_2$ front whereas changes in downdip fluid chemistry are dominated by the arrival of dense saline fluid from the injection well. Sigmoidal fronts in fluid chemistry are observed in the updip production wells, and correlate with changes in fluid temperature, a measure of CO$_2$ breakthrough. Elevated concentrations of divalent cations (Ca$^{2+}$, Mg$^{2+}$, Sr$^{2+}$, Fe$^{2+}$ and Mn$^{2+}$), in excess of the original pore fluid and injected water, are thought to represent dissolution of carbonate minerals in the reservoir which drives neutralization of fluid acidity and progressively increasing fluid alkalinity.


Multiple sulfur isotope fractionation during sulfur cycling in a warm, monomictic lake with sub-millimolar sulfate concentration

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Sub-millimolar concentrations of sulfate likely prevailed in the Archean Ocean. We studied the concentrations and quadruple isotope fractionation of sulfur species in the warm, monomictic Lake Kinneret (Tiberias), which has sulfate concentrations of $<$600 µM. The highest concentrations of zero-valent sulfur (ZVS), thiosulfate and sulfate occurred at concentrations $<$600 µM. The highest concentrations of zero-valent sulfur (ZVS), thiosulfate and sulfate occurred at concentrations of 5.0 µM, 1.35 µM and 0.76 µM, respectively.

In the vicinity of the RTZ, the $\delta^{34}$S fractionations between sulfide and sulfate are small (-17 – -21‰), with large positive $\Delta^{34}$S values (0.067 – 0.086 ‰), and can be attributed to sulfate reduction. ZVS is 0.1 – 4.7‰ more enriched in $^{34}$S than sulfide, consistent with equilibrium isotope effects between sulfide – polysulfide – rhombic sulfur and fractionation via phototrophic sulfide oxidation.

In the deeper waters, $\delta^{34}$S fractionations between sulfide and sulfate are large (-37 – -44‰), with smaller differences in $\Delta^{34}$S (0.009 – 0.073‰). Sulfur isotope values near the bottom of the lake can be explained by a combination of sulfate reduction and sulfur compounds disproportionation. High sulfur isotope fractionation is supported in this system even at very low sulfate concentrations by both the absence of sulfide scavenging by dissolved Fe (II) and the presence of the RTZ, where sulfide oxidation supplies zero-valent sulfur to deeper sulfidic waters.

Mineralogical and geochemical studies of the metasomatic rocks within Gachin, Kalat, Pohl and Hormuz Island salt plugs, Iran

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The Gachin, Kalat, Pohl and Hormuz Island salt domes are located in the Bandar Abbas province. They are a part of the Hormuz formation which situated in the Iran-Pakistan salt basin. The studied area centered at 25° 34’-27° 08’ N and 53° 55’-59° 15’ E at the geology map of the area [4]. The studied area is composed of some Infracambrian-Cambrian igneous and evaporites rocks. The igneous rocks composed of mafic to felsic composition and involve basalt, andesite, rhyolite, rhyolitic tuff and some hypabyssal bodies and occur in the within plate continental rift. On the basis of petrographic studies mineral assemblage has formed in magmatic (I) and metasomatic (II) stages. Clinopyroxene, amphibole, biotite, plagioclase,feldspar and quartz is the main magmatic minerals. Tremolite-actinolite, garnet, albite, epidote, sphen have occur in the metasomatic stage. According to the EPM analysis the chemical composition of the pyroxene is salite-frassalite to augite. The composition of garnet is andradite-grossular (An0.21 GROS0.78), feldspar is albite (An4.03-Ab95.36-Or0.60), epidote is pistachit. Clinopyroxene thermo-barometers range from 1060°C ±1290°C and 1 ≤ Ps ≤10 kbar [5], also chlorite [3] and plagioclase [2] geothermometer yielded a temperature of 330°C and 500°C for them respectively. Fluid inclusion studies have documented vapor bubbles, fluid and solid (cube halite) inclusions in the hydrothermal vein quartz. The salinity of the studied samples is 35-45 wt % NaCl and the homogenization temperature range 205°C-320°C. Fluid inclusion data on the mixing magmatic-meteoric field. On the basis of field, petrography, mineral chemistry, thermo-barometry and fluid inclusion data we could proposed following conclusions:

1. At first stage, magmatic and evaporite rocks have formed in the within plate continental crust in the striking an aborted rift. At latter stage, meteoric water entering igneous-evaporite assemblage and a hydrothermal system has created so Na, Ca, Fe metasomatism occurred in the system and metasomatic minerals have formed.

Carbon cycling in the Pliocene Velenje Coal Basin, Slovenia, inferred from stable carbon isotopes

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Introduction

In this study, stable isotopes of carbon were used to trace organic and inorganic carbon cycles and biogeochemical processes, especially methanogenesis within different geological media of the Pliocene lignite-bearing Velenje Basin in northern Slovenia. The study is based on investigations of carbon isotopic composition of the following geological media: 1) lithotypes of lignite, 2) coalbed gasses, 3) calcified woods and carbonate-rich sediments, and 4) groundwaters in various aquifers.

Discussion of Results

For different lignite lithotypes it was found that δ¹³C values ranged from -28.1 to -23.0‰, the variability is being a consequence of original isotopic heterogeneity of the source plant ingredients and of biogeochemical processes (gelification, fusinitization, mineralization of organic matter). In the lignite seam the major gas components were found to be CO₂ and CH₄ with small amounts of N₂. The carbon isotope compositions of carbon in CO₂ (δ¹³CCO₂) and CH₄ (δ¹³CCH₄) were very variable and ranged from -9.7 to 0.6‰ and from -70.5 to -53.2‰, respectively. The presence of thermogenic gases is unlikely due to the low rank of the coal and lack of higher chain hydrocarbons. Calcified xylite enriched with δ¹³C (δ¹³CCO₂ values up to 17.1‰) indicated that CO₂ reduction process was present at the time of formation of the basin. The δ¹³CCO₂ values (from -17.4 to -3.2‰) of groundwaters recharging the basin from the Triassic aquifer were consistent with degradation of organic matter and dissolution of dolomite. Groundwaters from the Pliocene sandy and Lithothamnium carbonate aquifers had δ¹³CCO₂ values (from -9.1 to 0.2‰) suggestive of degradation of organic matter and biogenic CO₂ reduction.


Mineralogical Magazine www.minersoc.org
Physical and chemical state of Fe-phases in Chinese aeolian dust

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Iron supplied by aeolian dust is a factor controlling the biomass of phytoplankton in high nutrient low chlorophyll (HNLC) regions, and dissolved Fe-stimulated biogeochemical activity can consume a large amount of CO2 in atmosphere, which may have a significant impact on the global C-cycle. In order to understand the physical and chemical state of Fe in the asian dusts, aerosol samples collected in Fukuoka, Japan and Hefei, China in March 2010 have been investigated in detail from nano to bulk scale. The analytical techniques include an inductively coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). A sequential extraction of the Fe-phase was also performed based on the previous method [1].

The Fe concentrations in the Hefei and Fukuoka samples during the dust event are 11.8 and 4.31 times higher than that in the Fukuoka sample in the non-dust period. The fraction of Fe-phase (in wt.% = mass of Fe in each Fe-phase/total mass of Fe) in the Fukuoka dust samples determined by the sequential extraction is Fe-bearing sheet silicate (59-61%), hematite and goethite (23-28%), ferrihydrite (7.5-12%), magnetite (3.0-4.3%). The XRD pattern indicates that illite and chlorite are the major Fe-bearing minerals in all samples. TEM observation reveals that aggregates of nano-sized ferrihydrite are present on the surface of illite.

Based on the solubilities of clays (4%) and Fe oxides (<1%) reported in the previous study [2] combined with our data, it is suggested that the clay minerals in the Chinese dust contribute predominantly to the Fe flux to the HNLC, which can potentially supply >6 times greater amount of Fe than that from Fe oxides [2]. It should be also noted that the ~10% of Fe present as ferrihydrite may be an important contribution because it is readily consumed by some photosynthetic algae species [3]. Still, quantitative investigation of highly bioavailable and soluble minerals in dust materials such as demonstrated in the present study should be essential to the appropriate evaluation of the impact of atmospheric Fe input into HNLC region.

References:


Uniqueness of kimberlite magma: Its source characteristics and transportaion systems revealed by isotope signatures

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Since kimberlite magma carries diamonds as xenoliths, it has been regarded to be formed at a depth of at least more than 150km and extruded to the surface within a few hours from the bottom of continental lithosphere. Based on Sr-Nd isotope systematics, kimberlites are classified into Group I and Group II [1]. Among them, Group I kimberlites show especially significant isotope signatures, which would reflect unique source characteristics and transportaion systems.

In the Sr-Nd and Nd-Hf isotope diagrams expressed as delta values, Group I kimberlites from different sites cluster close to the Bulk Earth values [2], while chondrite-normalized REE patterns show highly fractionated trend with L-REE enrichment. This implies that such high L-REE enrichment in a kimberlite magma should have occurred in the latest stage of magma transportaion system before eruption. To explain such high enrichment of L-REE, very small amount of partial melting of less than 1% is required. On the other hand, cluster of isotope signatures in Sr-Nd and Nd-Hf diagrams needs homogenization of magma source materials. Those isotope values mentioned above are often regarded to be a result of mixture between depleted (asthenosphere) and enriched (lithosphere) components. However, it seems quite difficult to attribute the cluster of isotope values of kimberlites with different sites and times to the process of small degree of partial melting. Our findings of high 3He/4He for Greenland kimberlites [3] and Ne isotope systematics for Russian kimberlites [4] definitely suggest that kimberlites (Group I) magma source materials have similar isotope signatures with those of OIBs and would possibly be located in the lower mantle. Although He and Ne isotopes show a sign of interaction with lithospheric components before eruption, it would be only effective for He and Ne due to their higher diffusivity compared to that of solid elements. Hence, the cluster of Sr, Nd, Hf isotopes of kimberlites (Group I) would reflect the chratacteristics of source materials of magma in the less fractionated deep mantle.

References:

Seasonal distribution and effects of herbicides on coral reefs around Okinawa, Japan

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Introduction
It is apprehensive about future degradation of coral reef caused by artificial chemicals such as herbicide and pesticides. Diuron [N’-(3, 4-dichlorophenyl)-N, N-dimethylurea] is one of the active substance contained in a herbicide. The used amount of diuron in Okinawa is the second highest in Japan [1]. Moreover, diuron has been using recently for antifoulant of ships as a replacement for organotin compounds. We investigated seasonal variation of herbicide contained in water and sediment around coral reef area in Ishigaki Island in Okinawa Japan, and carried out experiments to see the effect of the herbicide on coral metabolisms of photosynthesis and calcification.

Materials and Methods
Samples from twelve stations in the Shiraho lagoon and five in the Todoroki river were taken seasonally from August 2010 to May 2011. Diuron and other active substances were extracted using a solid-phase column and measured with a liquid chromatography with tandem mass spectrometry (LC–MS/MS).

Results and Discussion
Higher diuron of 222 ng/L was detected at the headwater of the Todoroki river in August. It decreased to 85 ng/L toward the river mouth. However, diuron in seawater and sediments at lagoon were significantly low level compared to the river. Because herbicide is mainly used in July to September in Okinawa and ground water from the catchment area flows geometrically to the headwater, the highest concentration was detected during summer season. The concentration in the lagoon has not reached to the level at which metabolic activity of coral colony is degraded.


Coral records of ocean acidification and physiological processes in the southern Great Barrier Reef

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Ocean acidification, the process of declining seawater pH due to increased uptake of CO2 from anthropogenic emissions, is likely to have severe impacts on marine calcifiers and related ecosystems. However, long-term records of ocean acidification from marine biota have rarely been evaluated. Here, we present high-resolution records of boron isotopic compositions (δ11B) as a paleo-pH proxy and calcification rates from two Porites corals (over 150 year old) from the southern limits of the Great Barrier Reef, Australia.

Carbon isotopes (δ13C) and trace element ratios (Mg/Ca and Sr/Ca) were also determined. The results from coral boron isotopic systematics show the obvious impact of enhanced uptake of anthropogenic CO2 on the ocean chemistry, resulting in a trend of decreasing seawater pH (-0.0016 ± 0.0002 pH unit yr-1) and decreasing δ13C compositions (-0.015 ± 0.002 ‰ yr-1 since 1960) due to fossil fuel burning (Suess effect). Ocean warming is also observed in the coral skeleton Sr/Ca record with slightly increased measured annual calcification from both corals during the observed period. This indicates that warming of the surface oceans may be countering the effect of decrease in carbonate ion concentration on coral calcification rates. Evidence of kinetic effects during coral calcification was also found in the long-term record; strong negative and positive correlation of coral growth with detrended δ13C and Mg/Ca. This suggests that CO2 hydroxylation is a dominant reaction in high calcifying conditions resulting in depleted δ13C. Also higher rate of coral growth could generate the kinetic effect on Mg partitioning and lead to greater incorporation into the aragonite skeleton of corals.
Validation of saltation flux parameterization with observation

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Introduction
The estimation of natural dust emission amount is important to understand the effects of dust on climate. Many dust emission parameterizations have been developed and it is required to investigate emission parameterizations and validate them with observation data.

Results and Discussion
In this study, the saltation flux formulation given by White [1] is used and it is as follows:

\[ Q = C \rho_a g \frac{u^3}{x} \left(1 - \frac{u_t}{u_*} \right)^2 \left(1 + \left(\frac{u_t}{u_*}\right)^2\right) \]

where \( C \) is coefficient, \( \rho_a \) and \( g \) are air density and gravity, respectively, and \( u_* \) is friction velocity, \( u_t \) is threshold friction velocity. The White equation [1] is compared with observation data collected during the Japanese Australian Dust Experiment (JADE) [2]. The coefficient \( C \) is obtained by the iterative method to make the difference between observed and calculated fluxes minimize. Figure 1 shows the comparison of calculated flux using new linear coefficient with observation data. The result indicates that the saltation flux equation has a good ability to predict sand flux with tuning the linear coefficient only.

![Figure 1](image_url)

**Figure 1:** (a) Observed and calculated \( Q \) with friction velocity, (b) Scatter plot of observed \( Q \) versus calculated \( Q \).


Geochronology and geochemistry of Hongqilapu granite in eastern Pamirs, China

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Hongqilapu granite is distributed in the boundary of China and Pakistan, composed of granodiorite and quartz diorite which developing dioritic enclave. The granite belongs to the sub-aluminum to peraluminous and calc-alkali series, and is characterized by rich in Al, Fe, Ca, and LILEs (Rb, Ba, Th), poor in Hf, Zr, Y, Yb. In particular, partial rock have the geochemistry character of adakite, such as \( \text{SiO}_2 = 60.41 \times 10^2 - 72.02 \times 10^2 \), \( \text{Al}_2\text{O}_3 = 15.53 \times 10^2 - 16.13 \times 10^2 \), \( \text{MgO} = 0.66 - 2.56 \times 10^2 \), \( \text{Y} = 9.61 - 18 \times 10^2 \), \( \text{Yb} = 0.8 - 1.44 \times 10^2 \), \( \text{Sr} = 393 - 560 \times 10^2 \), riching LREE, HFSEs’ (Ti, Nb, Ta) content is as much as, Eu have negative anomaly faintly. In addition, these rocks’ \( \text{K}_2\text{O}/\text{Na}_2\text{O} > 1 \) and \( \text{Sr-Y-Zr} \) diagram show that them belong to C-form adakite with high kalium, proving that Hongqilapu granite is the production of thickened lower crust partial melting. LA-ICP-MS zircon U-Pb dating of the granite indicate that the weighted mean \( ^{206}\text{Pb}^{238}\text{U} \) age are 107.20±0.76Ma (n=29, MSWD=1.09), which belongs to Early Cretaceous Epoch. In conclusion, these information show Bangonghu-Nujiang ocean basin of Neotethys had closed earlier than lower cretaceous, which provide a new valuable information on the time limit of colliding between Gangdise block and Qiangtang massif.
The Paleozoic minimum in $^{87}$Sr/$^{86}$Sr ratio in the Capitanian (Middle Permian): Records from the mid-Panthalassa paleo-atoll limestones

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We report a detailed secular change of the Middle-Late Permian seawater $^{87}$Sr/$^{86}$Sr ratio with the unique ‘Permian minimum’ interval detected in mid-Panthalassa (superocean) paleo-atoll carbonates. The analyzed limestones at Kamura and Akasaka sections in Japan occur as exotic blocks within the Jurassic accretionary complex. On the basis of fusuline biostratigraphy, both sections span across the Middle-Upper Permian or the Guadalupian-Lopingian (G-L) boundary characterized by a major biotic crisis. Two sections are separated from each other for 500 km at present, thus were likely derived from different paleo-seamounts existed in mid-Panthalassa.

A 30 m-thick interval with low $^{87}$Sr/$^{86}$Sr value (< 0.7070) was detected in the Capitanian (Upper Guadalupian) interval, i.e. the Yabeina (fusuline) Zone, Lepidolina Zone, and the barren interval in the Kamura section. Data from Akasaka section confirm that extremely low $^{87}$Sr/$^{86}$Sr values (0.70688) similarly characterize the Yabeina Zone and the barren interval. A remarkable rise in $^{87}$Sr/$^{86}$Sr values for 0.00073 up to 0.70761 occurred in the barren interval after the ‘Permian minimum’ in both sections, suggesting a general isotopic trend in the superocean. This increase in Sr isotope after the ‘Permian minimum’ likely suggests that a huge amount of highly radiogenic terrigenous clastics have been shed into Panthalassa by connecting intra-Pangean drainage systems directly to the superocean. The development of the new drainage systems might be related to large-scale continental rifting, thus the initial breakup of Pangea. It is noteworthy that carbonate stable carbon isotope ratio (δ13C_carb) also shifted dramatically in the latest Capitanian barren interval immediately before the G-LB.

Fe(II) oxidation under very low O2 conditions: New rate law and its implication

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Many geological proxies point the great rise of atmospheric oxygen in the Paleoproterozoic (Great Oxidation Event). The proxies including mass independent fractionation in sulfur isotopes reveal that atmospheric oxygen increased from very low concentration (< ~10^-5 atm of pO2) to low concentration (> ~10^-3 atm of pO2) between 2.5 and 2.0 Ga. However, many of the proxies are useful for deciphering the timing of the transition in pO2 levels rather than its quantitative pattern. On the other hand, paleosols formed during the Paleoproterozoic have recorded the ratios of Fe (III)/Fe (II) at the time of their formation and these kinetical data can give more quantitative estimates of pO2. To quantitatively estimate pO2 through the ratios of Fe (III)/Fe (II), the rate law of Fe (II) oxidation should be understood.

Experimental data of Fe (II) oxidation have been obtained under the conditions of pO2 = 10^-3 - 10^-5 atm and pH = 7.57 - 8.12. Combined with previous oxidation data at pO2 > 10^-3 atm, newly discovered is that the rate law changes its form from d [Fe (II)]/dt = - k [Fe (II)][OH^-]^2 [O2] at pO2 > ~5 x 10^-3 atm to d [Fe (II)]/dt = - k' [Fe (II)][OH^-]^0.55 [O2] under the conditions of pO2 = 5 x 10^-3 - 10^-5 atm.

In interpretation of this new rate law, especially the change in the power of [O2] from 1 to 0.55, we suggest that under the very low O2 conditions intermediate oxygen species (superoxide, hydrogen peroxide and hydroxyl radical) attack Fe (II) more effectively, which results in faster Fe (II) oxidation rate than previously considered. Out of possible reactions that produce oxygen species from oxygen, the reaction,

$$O_2 + (18/11)H_2O = (16/11)H_2O_2 + (4/11)HO_2$$

gives the power of [O2] of 0.55. Combination of this reaction and those proposed by Haber and Weiss reproduces the experimental results well under the conditions of 10^-2 - 0.2 atm of pO2.

The new rate law was applied to the ratios of Fe (III)/Fe (II) of paleosols formed during the Paleoproterozoic, revealing that atmospheric oxygen increased gradually, linearly on the logarithmic scale, from < ~ 10^8 to > ~ 10^11 atm of pO2 between 2.5 and 2.0 Ga.
Primary structures, petrography and geochemistry of Deccan flood basalts at Anantagiri Hills, Andhra Pradesh, India

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The Cretaceous age Deccan flood basalts of Anantagiri Hills in south India represented by six lava flows show formation of columnar joint zones as the most conspicuous feature in each basalt flow unit. These flow units, exhibiting columnar structures, enable division into three well defined zones namely: Lower Colonnade Zone (LCZ); Middle Entablature Zone (MEZ) and Upper Colonnade Zone (UCZ). The columns in UCZ are five sided; MEZ separating the UCZ and the LCZ displays four sided intersecting, fanning and fragmented columns while the underlying LEZ has four to five sided vertical columns. These basalts show a mild affinity towards basaltic andesite on the TA S (Na₂O+K₂O vs. SiO₂) diagram, while in the Al-Fe+Ti-Mg ternary plot these basalts plot in the iron rich tholeiitic field. The major and trace element signatures of these tholeiitic basalts are similar to that of the Ambenali Formation basalts, suggesting possible extension of this Formation in SE Deccan Volcanic Province. REE plots define a nearly flat pattern with mild LREE enrichment and negative Eu anomaly. Primitive mantle normalized multielement patterns show mild LREE, LILE troughs positive Ba, Nb and Pb peaks and negative K, Sr and P anomalies in similarity with plume type CFB’S. The well developed sequence of colonnade structures in the different basalt flow units in Anantagiri Hills appear to have formed due to conductive cooling initiated both from the top and bottom portions of these flows. Geochemical signatures shown by these tholeiitic basalt flows suggest that the precursor was probably generated by low degree partial melting of an enriched mantle source.

Ectomycorrhizal fungi and silicate mineral weathering: Characterising nanoscale interactions using AFM

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Ectomycorrhizal (ECM) fungi substantially affect mineral weathering [1, 2]. In order to understand the nanoscale processes occurring at the fungi-mineral interface, we have used Atomic Force Microscopy (AFM) to investigate the interactions of three Suillus ECM fungi, S. bovinus, S. luteus and S. variegatus, with sheet silicate minerals.

After 2-3 months of incubation under controlled laboratory conditions, the fungal hyphae and the mineral surface were imaged to nanometre resolution. To assess the effect of the fungi-mineral interaction on the mineral surface, a cleaning procedure was applied to biotite flakes colonised with S. luteus; this removed the organic material and exposed the ‘reacted’ mineral surface for further analysis. The cleaning protocol was also performed on a biotite control.

Our results show that all three Suillus species generate a large amount of organic material, forming typically a 1-5 nm thick coating on the mineral surface extending over many tens of microns. We have previously observed a similar ‘biolayer’ with Paxillus involutus [3]. AFM images of the cleaned biotite surface (Fig 1a), and the control biotite surface (Fig. 1b), show that both displayed a domain-like surface morphology. However, only on the fungi-colonised surface were round pits found, about 100 nm across and 5 nm in depth (Fig. 1a). These results indicate that the surface pitting is linked to the colonisation of the mineral with S. luteus.

Figure 1: AFM images of a cleaned biotite surface: a) previously Suillus luteus colonised flake, note the pitting; b) control flake; field of view 8x8 µm, inserts 2.5x2.5 µm.

A $^{13}$C DOC tracer approach to estimate the contribution of semi-labile dissolved organic carbon to stream ecosystem metabolism

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$^{13}$C Tracer Method

In streams and rivers, dissolved organic carbon (DOC) supplies energy and carbon (C) to heterotrophic bacteria. The complexity of the DOC pool combined with simultaneous processes that continually produce, transform and consume DOC molecules in transport, makes in situ measurements of DOC uptake challenging. A tracer approach is a logical solution and we prepared a $^{13}$C tracer of semi-labile DOC from soil-aged $^{13}$C-labeled Liriodendron tulipifera tissues with a chemical composition reflective of the heterogeneity of terrestrially produced C that has been modified by sorptive fractionation onto mineral surfaces and oxidation by soil bacteria.

Results

We used the tracer in a whole-stream injection coupled with bioreactor-based lability profiling to measure an uptake length of 4.5 km for semi-labile DOC constituents in a headwater piedmont stream and estimate support of ~10% of ecosystem metabolism.

Figure 1: A. Whole-stream addition $^{13}$C uptake; B. Lability profiles of stream water DOC (open) and $^{13}$C tracer (solid).

Biogenic Fe(III) minerals lower the efficiency of iron-mineral-based commercial filter systems for arsenic removal

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Millions of people worldwide are affected by As-contaminated groundwater. Since abiogenic and biogenic Fe (III) (oxy)hydroxides sorb/co-precipitate As efficiently [1], filter systems containing Fe (III) minerals are applied to purify As-contaminated water. However, commercial filters containing abiotic Fe (III) (oxy)hydroxides (granular ferric hydroxide, GFH) showed varying As removal efficiency depending on groundwater geochemistry and it was unclear whether Fe (II)-oxidizing bacteria influenced their efficiency. We found up to $10^7$ Fe (II)-oxidizing bacteria/g dry weight in GFH-filters and determined the performance of the filters in the presence and absence of Fe (II)-oxidizing bacteria. GFH-material sorbed 1.7 mmol As (V)/g Fe. This was ~8 times more efficient than biogenic Fe (III) minerals alone that sorbed 208.3 µmol As (V)/g Fe. It was also ~5 times more efficient than a 10:1 mixture of GFH-material and biogenic Fe (III) minerals that bound 322.6 µmol As (V)/g Fe. Co-precipitation of As (V) with biogenic Fe (III) minerals in the absence of GFH-material removed 343.0 µmol As (V)/g Fe. As removal by co-precipitation with biogenic Fe (III) oxides in the presence of GFH-material bound 1.5 mmol As (V)/g Fe. This was slightly less efficient as by GFH-material alone. Since the formation of biogenic Fe (III) minerals lowers rather than increases the As removal efficiency of the filters, we recommend to exclude microorganisms from the filters (e.g. by activated carbon filters) to maintain their high As removal capacity.

Pressure-temperature diagenesis of Fe minerals and biomass produces hematite, siderite and magnetite as present in Banded Iron Formations

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The reconstruction of microbial life in ancient sedimentary deposits is complicated by the influence of temperature and pressure during diagenesis and metamorphism. While minerals and persistent organic molecules may be evident in ancient rock formations such as Banded Iron Formations (BIFs), the specific primary minerals, their (trans-)formation mechanisms and proposed microbial processes involved are not certain. Understanding the transformation of biogenic iron minerals is the key to constraining models of BIF deposition that occurred between 3.8-0.8 billion years ago [1]. Thermal and barometric transformations of Fe (III) minerals associated with organic carbon (biomass, e.g. microbial cells) have not yet been systematically tested in laboratory experiments. Here, we present experimental results of mineral transformations of Fe (III) hydroxide and organic matter (glucose as a proxy for biomass) in gold capsules at elevated pressures and temperatures. Iron speciation and mineralogical analysis show the conversion of ferrihydrite [Fe(OH)3, ferric hydroxide] into hematite (Fe2O3), magnetite (Fe3Fe2O4), and siderite (Fe5CO3). Our results suggest that the joint precipitation of iron form, i.e. Fe (III) is partially reduced, under diagenetic conditions decoupled from conditions in the ocean/atmosphere. The experimental system presented herein offers a means to bridge the gap between geological evidence from the field and laboratory experiments with modern microbe analogues.


Source rock-oil correlation in the Sinop Basin (Northern Turkey)

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Lower Cretaceous aged Çağlayan Formation is exposed in the Sinop Basin consists of black coloured claystone, siltstone, shale and marl, and has source rock characteristics. An oil seep from Çağlayan Formation is located in the Ekinveren region of the Sinop Basin.

The average total organic carbon (TOC) values of the shale samples from the Çağlayan Formation in the Ekinveren and the Bûrûnik locations are 1.48, 1.26 % and HI values are 190, 244 mg HC/g TOC, respectively. The potential yield values of the sample from the Ekinveren and the Bûrûnik are >2 mg HC/g rock and these potential yield values indicate fair hydrocarbon potential for the Çağlayan Formation.

The unimodal n-alkane distribution with lower carbon number dominant is observed in the gas chromatograms of the shale samples from the Çağlayan Formation in the Ekinveren and the Bûrûnik locations. Low TAR, (C19+C20)/C23 tricyclic terpane ratios and type II kerogen content indicate that the shale samples from the Çağlayan Formation comprise dominantly marine organic matter. Pr/Ph ratios for the Ekinveren and the Bûrûnik shale samples are 1.39 and 0.89, respectively.

Average Tmax values for the Ekinveren and the Bûrûnik locations are 429 and 433°C, respectively. According to Tmax data, Çağlayan Formation has immature-early mature characteristics in the Ekinveren location and early mature-mature characteristics in the Bûrûnik location. CPI values, isoprenoid/n-alkane ratio, 20S/(20S+20R) and ββ/(ββ+αα) C29 sterane, 22S/(22S+22R) C29 homohopane ratios for the Ekinveren and Bûrûnik shale show that Bûrûnik shale are more mature than those of the Ekinveren shale. A large UCM and n-alkanes, isoprenoids that were recorded in low amount in gas chromatogram for oil sample from the Ekinveren seep indicate that the Ekinveren oil seep were heavily biodegraded. Similar tricyclic terpane, C24 tetracyclic terpan, norhopane, hopane and homohopane distributions were recorded in m/z 191 and m/z 127 mass chromatograms of samples from the Çağlayan Formation and the Ekinveren oil seep. Higher diasterane and pregnane content is typical for oil and shale samples. C27, C28, C29 sterane distribution for oil and shale samples is similar. According to biomarker data, Çağlayan Formation and Ekinveren oil seep are well correlated to each other.
Mineralogical and chemical variations in kaolin and alunite deposits in vicinity of the Aksaray region (Central Anatolia, Turkey)

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The kaolin-alunite deposits were formed in Lower Miocene volcanic and volcanoclastic, mostly dacitic, rhyodacitic, and andesitic rocks. The deposits were derived from by supergene and hypogene alteration processes. Kaolinite/halloysite is clay minerals, sometimes pure and sometimes associated with α-quartz, K-feldspar, plagioclase, alunite, natroalunite and hematite, whereas other kaolinite accompanies smectite, which represents a moderate kaolinization. Massive zones of alunite deposits sometimes pure, and show gradational passing to kaolinite/halloysite, and they were cut by gypsum and native sulphur veins and contain partially cinnabar and realgar mottles and/or veinlet. Tridymite and rarely low-cristobalite are the dominant silica mineral in these kaolins. Barite, pyrophyllite, minamiiite, hematite, and geotite/lepidocrocite are rarely observed. Bentonite deposits composed mainly of nearly pure Ca-montmorillonite, observed as gradually or sharply at the uppermost levels or lateral sides of the alunite and kaolinite deposits. The alunite and most of kaolinite are products of hypogene alteration. Alunite, kaolinite, and gypsum samples show very similar chondrite-normalized REE trends, suggesting that they may be linked to common source. The REE patterns of the alunite and kaolinite samples are characterized by strong LREE enrichment ((La/Lu)c=54.7 and 170.5, whereas gypsum and bentonite samples show moderate enrichment (9.2 and 7.2), respectively. Most of the alunite and kaolinite samples have pronounced positive Eu anomalies (1.08) and gypsum and bentonite samples negative and/or weakly negative Eu anomalies ranging from 0.77 to 0.89. All of the samples have positive Ce anomalies. Alunite and native sulphur samples from the deposits have δ^34S values of 5.03-6.62%, and 5.97-7.49%, respectively, with values for gypsum of 4.5-5.24%. Therefore, the sulphur-rich minerals may have been formed by steam-heated hydrothermal environments. The isotopically slightly heavy sulphur in the minerals could be derived from H_2SO_4. Development of the hydrothermal alteration contemporaneous with extensional tectonic and strike-slip faulting movements have resulted in hypogene alunite and kaolinite deposits. Hydrothermal alteration strongly affected along fault zones but subsequent weathering (supergene) away from the fault zones, and much of the volcanoclastic rocks have been altered to a more smectite-rich and less kaolinite-bearing assemblage.

A new model of the asthenosphere

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Although the classic model of asthenosphere = a layer of partial melt has been questioned for more than two decades, such a model is revived recently based on seismological observations showing a sharp and large reduction in seismic wave velocity. In this presentation, I will argue that such a model is not consistent with physics of behavior of partially molten materials nor with the seismological observations. First, in the gravity field, it is difficult to maintain a substantial amount of melt for a geologic time scale. Layering observed in some lab experiments is often invoked to explain the persistency of a melt-rich layer, but the lab experiments show ~20° tilt and hence the melt-rich layer will be compacted. Second, if a large reduction of velocity (~5-10%) were to be due to the presence of sub-horizontal melt-rich layer, then the asthenosphere should show large anisotropy in SH/SV waves (5-10%), which is not observed.

I propose that the basic properties of the asthenosphere is best explained as a residue of partial melting near the 410-km discontinuity. Partial melting removes a large fraction of incompatible elements leading to the ‘depleted’ homogenous composition, and also leads to ~0.01 wt% of water in the asthenosphere. The lab data show that this much of water is consistent with the observed electrical conductivity of the asthenosphere including its regional variation. If water reduces the strength of grain-boundaries, it can easily explain the sharp drop in velocity as much as ~10%.
Sequential extraction of Pb, Zn, Cd, and Cu in contaminated soils due to mining operation in Isfahan-Iran

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Sequential extraction was applied on 6 soil samples collected from metal contaminated site due to Gooshfil mining operation (20 km south west of Isfahan) to evaluate the level of contamination and bioavailability of Pb, Zn, Cd, and Cu. The sequential extraction method which was used in this research has been introduced by Tesser et al. in 1979 and modified by Salbu et al. in 1998. This method separates metals in six operationally defined fractions: water soluble, exchangeable, carbonate bonds, oxides bonds, organic bonds and residual fractions.

From the results of this study it can be concluded that the study area is contaminated with lead. Zn is lower but near the contamination level. Mining operation in the area is the major source of metal contamination. The results obtained from the sequential extraction indicate that up to 90% of metals in soil samples were associated to low soluble and high stable fraction such as oxide, organic and residual fraction. Metal distribution in soil samples generally followed the order oxide fraction > residual fraction > organic fraction > carbonate fraction > exchangeable > water-soluble.

Metal mobility and bioavailability

Ratio of relatively metal bioavailable and mobile fractions to stable and less mobile fractions is defined as mobility factor.

Metal mobility factor (Mf) defined as the following equation:

\[
Mf = \frac{(\text{water-soluble} + \text{exchangeable} + \text{carbonate fraction})}{\text{total metal content}} \times 100
\]

The high Mf values have been interpreted of relatively high biological availability and bioaccessibility of metals in soils. Mobility factor for six soil samples was determined by using the result of sequential extraction. Results are presented in Table 1.

Table 1: Mobility factor for metals

<table>
<thead>
<tr>
<th>Soil</th>
<th>Pb</th>
<th>Cd</th>
<th>Zn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1.8</td>
<td>7.8</td>
<td>1.7</td>
<td>2.0</td>
</tr>
<tr>
<td>S2</td>
<td>0.7</td>
<td>6.9</td>
<td>0.6</td>
<td>0.7</td>
</tr>
<tr>
<td>S3</td>
<td>3.0</td>
<td>9.7</td>
<td>1.0</td>
<td>3.6</td>
</tr>
<tr>
<td>S4</td>
<td>3.9</td>
<td>10.2</td>
<td>1.4</td>
<td>8.1</td>
</tr>
<tr>
<td>S5</td>
<td>1.9</td>
<td>9.7</td>
<td>2.0</td>
<td>7.1</td>
</tr>
<tr>
<td>S6</td>
<td>3.1</td>
<td>10.2</td>
<td>1.0</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Bioavailability for metals found to be very low. Metal mobility factor for four studied metals were lower than 12%. The highest mobility was measured for cadmium and the lowest obtained for Zn. The results of bioavailability and mobility factor for the studied metals in the soil samples generally show the following order: Cd >> Cu >> Pb > Zn

Viscosity of MgO-SiO$_2$ melt system from first principles simulations

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Transport properties of silicate melts are crucial to our understanding of chemical and thermal evolution of Earth. In recent years, we have performed density functional theory-based molecular dynamics simulations to study from first principles several key properties including viscosity ($\eta$) of relevant melts in the MgO-SiO$_2$ system. Numerous simulations of durations from a couple of tens of picoseconds to a few nanoseconds were completed to sample the pressure-temperature-composition ($P$-$T$-$X$) space accurately. The calculated results show that the viscosity is strongly dependent on pressure and temperature showing large deviation from the normal Arrhenian behaviour. The melt viscosity varies by two to three orders of magnitude across the entire mantle pressure regime. The predicted anomaly (i.e., viscosity increasing on compression) becomes more pronounced in silica-rich melts. Such dynamical changes can be associated to the structural changes. The simulations results were used to derive a viscosity model, $\eta$ ($P$-$T$-$X$), applicable for the parameter space considered. The predicted viscosities compare favourably with the available measured data.
Putting constraints on the life cycle of organic carbon based on ecosystem scale flux measurements

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Large quantities of volatile organic compounds (VOC) enter the atmosphere. The annual production of VOC (600 - 2000 TgC/a) likely exceeds that of methane and CO (~500 TgC/a each). Together these gases fuel tropospheric chemistry. Oxidation of VOC leads to the formation of aerosol [1] via complex organic chemistry [2, 3] in the gas and aerosol phase thereby modulating the oxidation capacity of the atmosphere [4]. It is currently believed that a large fraction of VOC originates from biogenic sources (e.g. >80%). The life cycle of organic carbon is ultimately controlled by emission and deposition processes at the surface. Uncertainties in budgets of VOC and potential ramifications for organic aerosol production in the atmosphere will be discussed based on a synthesis of direct VOC flux measurements performed in a range of different ecosystems. These direct flux measurements will be used to address some outstanding questions concerning (1) the amount of reactive biogenic organic aerosol precursors, (2) the magnitude of deposition processes and (3) the lifetime of reactive biogenic organic aerosol precursors in the atmosphere.


Molecular-level studies of Fe(III) in aquatic systems

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The fate and behavior of iron (Fe) in aquatic environments is highly dependent on chemical interactions with natural organic matter (NOM). There is however still limited knowledge about the molecular structure, strength and hydrolysis of the Fe species formed in association with aquatic NOM and few studies that present results obtained by molecular-level probes (e.g. [1, 2]). In this study we have used extended X-ray absorption fine structure (EXAFS) and Fourier transformed infrared (FTIR) spectroscopy in combination with chemical speciation modeling to characterize Fe (III) in different types of aquatic NOM and in dissolved and colloidal material in different size fractions from a boreal stream.

Our results show that Fe in association with NOM and fulvic acid from river water forms two predominant species; mononuclear Fe (III)-NOM complexes and polymeric Fe (III) (hydr)oxides. The distribution of the two species is largely dependent on pH and Fe concentration. The speciation in the boreal stream water is dominated by mononuclear organic Fe (III) complexes irrespective of pH and size fraction. In the organic complexes Fe is coordinated by carboxylic functional groups forming a structure consisting of five-membered chelate rings and these complexes are sufficiently strong to prevent hydrolytic polymerization of Fe even at pH 7.0.

Thus, in oxic aquatic environments, with organic matter present, the fate of Fe will to a large extent be controlled by the properties of the organic Fe (III) complexes. In addition, the stable Fe (III)-NOM complexes formed will have important implications for the biogeochemistry of other elements, such as phosphorus and arsenate, that are known to be strongly associated with Fe (III).

Temporal trend in anthropogenic sulfur aerosol transport from central and Eastern Europe to Israel

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Decrease of sulfur emissions in central and eastern Europe over the past 3 decades is well documented. These changes result in a decreasing trend of sulfate aerosol and aerosol forcing over the source region, but also at a receptor site located in southern Israel, thousands of kilometers downwind. A combination of several independent observations, namely, satellite and ground-based remote sensing, in situ aerosol sampling, and backward trajectory analysis, was implemented to show significant downward trends in fine particle aerosol optical thickness (AOT), in general, and sulfur aerosol, in particular. MODIS-Terra observations over central Europe show 38% reduction of fine AOT. At the reception site in southern Israel, 43% reduction of fine AOT was observed by a sunphotometer and 25% reduction of sampled fine aerosols was obtained. During the corresponding observation periods, the coarse mode AOT has remained constant. The majority of the backward trajectories, where meaningful sulfur events were observed at the receptor site, are originated from eastern and central Europe. The aerosol radiative effect at top of the atmosphere has become less negative during the past decade, decreasing by 30% in Europe and 67% in Israel.

Neoproterozoic ice ages, boron isotopes, and ocean acidification

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The Neoproterozoic Earth underwent at least two severe glaciations, each extending to low paleomagnetic latitudes and punctuating warmer climates. The two widespread older and younger Cryogenian glacial deposits in Namibia are directly overlain by cap carbonates deposited under inferred periods of high atmospheric carbon dioxide concentrations [1]. Oceanic uptake of carbon dioxide decreases ocean pH and here we present a record of Cryogenian inter-glacial ocean pH, based on boron isotopes in marine carbonates. Our data document characteristically different B isotope profiles of the two Cryogenian carbonate transects that are consistent with the presence of two ‘pan-glacial’ climate states, but indicate that each had its own distinct environmental conditions. The Marinoan interglacial δ11B profiles are systematic and remarkably consistent, and they vary by up to 11‰. This yields a relative pH variation of up to 1.5 pH units, and implies a pH of 8.5 at the onset of cap carbonate deposition, followed by a decrease in pH to ~7 and then a return to pH ~8 for the upper part of the section. The transient ocean acidification excursion and the alkaline pH condition near the start and termination of the inferred greenhouse state suggests a rapid draw-down of CO2 initiated at the start of the deglaciation and supports inferences of a thick, global sea-ice shield with minimal air-sea gas exchange during glaciation. In contrast, largely constant B isotope values for the Sturtian-aged glacial aftermath do not indicate extreme ocean pH (~8.3) conditions and do not support a contemporaneous major ocean acidification event and associated high pCO2 at the time of the older Cryogenian glaciation and deglaciation. That leads us to speculate that the ocean during the older glaciation was not totally frozen and that the hydrological cycle was functioning [2].

Molecular-scale mechanism of Mo isotopic fractionation during adsorption on ferromanganese oxides

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Molybdenum (Mo) shows a large mass-dependent isotopic fractionation during adsorption on ferromanganese oxides, which is responsible for isotopic composition of Mo in modern oxic seawater [1]. The aim of this study is to reveal the fractionation mechanisms of Mo isotopes during adsorption on natural ferromanganese oxides. We investigated surface complex structures of Mo on various Fe/Mn (oxyhydr)oxides, key factors for the isotopic fractionation, and compared them with previously-reported isotopic fractionation.

Our XAFS analysis showed that symmetry of surface Mo species is different from MoO$_4^{2-}$ (Td) in seawater in the case of its adsorption on some solids. This structural information showed the excellent correlation with the degree of isotopic fractionation of Mo reported in previous studies: the proportion of Oh species or their magnitude of distortion in surface Mo species becomes larger in the order of ferrihydrite < goethite < hematite < δ-MnO$_2$ [2], a trend identical to the degree of isotopic fractionation [3]. Based on the comparison with previous reports for surface Mo species on various oxides such as MgO, Al$_2$O$_3$, and TiO$_2$, the symmetric change from Td to Oh is suggested to be driven by the formation of inner-sphere complexes on specific sites of the oxide surfaces. In addition, the mode of attachment (inner- or outer-sphere) of surface Mo species is well correlated with the hydrolysis constant of the cation (e.g. Fe$^{3+}$ and Mn$^{4+}$) in oxides.


EPMA study of sulfides in ultramafic suites of J.C.pura belt, Western Dharwar craton, India

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Significant ultramafic magmatism has been recorded in the western part of the Dharwar craton, southern India. J.C.Pura schist belt is one such ultramafic milieu with abundant dunite and peridotite which have been extensively serpentinitised. Their komatiitic nature and extrusive mode of formation is evident from the field study. Some of the dunite bodies are chromitite in nature and contain veins and stringers of chromite. Highly altered bodies of chromitite show strong development of magnesite veins. They contain complex nickel sulfides which have been studied by ore microscopic method, besides analysing by EPMA. Camica (France Make) EPMA system was used for EPMA. Polished thin sections were prepared for this study and through a preliminary study the mineral-spots were marked for the EPMA studies. Selected representative samples from different rock types of dunite/peridotites, pyroxenites and cumulus schistose rocks were identified for this study. The chemical composition of different ore phases and the identified mineral phases are presented. From the analysis it is deciphered that cobalt-nickel-pyrite and pentlandite make the most abundant ore phase among the sulfides followed by pentlandite-pyrrohite-chalcopyrite assemblage. Occurrence of sulfides within the oxide phase (Chromite-Magnetite-ilmenite) is also noticed infrequently. This suggests to the possibility of sulfide evolution progressively with magma cooling. Strong immiscible and solid-solution relation are evident in the entire sulfide phase. The disseminated nature of them suggests to the possibility of poor sulfidation process during their formation i.e. either there was poor endowment of sulfur at the time of partial melting or during the ascent of magma through the crustal rocks. This is being reported for the first time for the J.C.Pura area. However detailed volcanic stratigraphy of the belt when studied, which is underway, and whole rock geochemistry including elemental stratigraphy of the belt when studied, which is underway, and whole rock geochemistry including elemental ratios integrated, it will provide more insight in to the actual potential of the sulfides especially Ni sulfides in the said belt.
Microbial activity in gas field fluids and in laboratory experiments simulating geological CO2 storage

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Microbial activity in gas field fluids from two natural gas fields in Germany was assessed for evaluation of possible biochemical transformation of injected CO2. 16S rDNA clone library construction revealed the presence of bacteria (Thermoanaerobacterium sp., Petrotoga sp., Desulfotomaculum sp.) in both gas fields and archaea (Methanolobus, Methanoculleus) in one gas field [1]. Gas field fluids of both fields contain free amino acids, polysaccharides, carbonic acids (formic acid, acetic acid) and alcohols (methanol, ethanol). Bio-molecules and metabolites form 25 to 50% of the total dissolved organic carbon of 2 to 10 µM. Moreover, both gas field fluids contain 0.1 to 250 µM dissolved H2.

Laboratory experiments for simulation of geological CO2 storage were conducted in high-pressure reactors (autoclaves) for 6 to 12 months. Gas field fluids and milled rock material from exploration drilling cores were reacted at pCO2=6.5 bar, pH2=3.5 bar, pN2=4 bar and T=40°C. During the experiments, cell numbers of the reactor fluids rose and CO2 and H2 were consumed. DOC concentrations increased up to several hundred mM, while its composition remained comparable to the gas field fluid DOC. For one gas field, sulphate reduction was observed. Fatty acids, saturated hydrocarbons and elemental sulphur (in sulphate reducing systems) were detected in the sediments after the experiment. Fluorescence microscopy was used for visualisation of polysaccharides, proteins and calcium in the sediment samples. Both protein-calcium and polysaccharide-calcium associations were detected. REM-EDX analysis revealed biogenic sulphides and carbonates in sulphate reducing systems. Microbial activity at simulated CO2 geological storage resulted in elevated concentrations of dissolved organic carbon, production of EPS and precipitation of biogenic minerals and thus might influence CO2-storage capacities and rock physical properties of CO2 storage units.


Analysis and application of water-rock-CO2 reaction using basalt to underground CO2 sequestration

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Water-rock-CO2 reaction attract attention in many parts of science. It consists of three following reactions:

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} &= \text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^- \quad (1) \\
\text{MSiO}_3 + 2\text{CO}_2 + \text{H}_2\text{O} &= \text{M}^{2+} + \text{H}_4\text{SiO}_4 + 2\text{HCO}_3^- \quad (2) \\
\text{M}^{2+} + 2\text{HCO}_3^- &= \text{MCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (3)
\end{align*}
\]

where M is bivalent metal ion.

There are two steps. First, CO2 dissolves in the water by (1) or mineral and water react CO2 by (2). Next, bivalent metal ion and hydrogen carbonate ion generate and carbonate minerals (MCO3) precipitate by (3).

We are applying them to the CO2 underground sequestration and the estimate of atmospheric CO2 concentration of Archean and formation of mineral water, and global carbon cycle in earth system. In this paper we will focus on CO2 underground sequestration based on experimental water-basalt-CO2 reaction and computer simulation.

Assessment of the nanoscopic dissolution rate of basic lead carbonate (hydrocerussite)

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Hydrocerussite (Pb3(CO3)2(OH)2), related to shannonite and plumbeous phases, is reported to be a characteristic secondary mineral [e.g. 1] particularly associated with the weathering of industrial metallic Pb (e.g. bullets, shots, pipes) and the oxidation of Pb-Zn-Ag ore deposits. Such processes exhibit a straightforward connection between the dissolution-precipitation of hydrocerussite (log Ksp=-43.7) and the mobility of Pb contaminants in the environment. Synthetic hydrocerussite (basic lead carbonate known as ‘white lead’ [e.g. 2]) has been broadly used in pigments and cosmetics. In this study, we present in situ AFM experiments that provide evidence of the nanoscopic reactivity behaviour of hydrocerussite {0001} surfaces in contact with deionized water. The AFM study shows that the edge pits, with initial depth ~1 nm, exhibit random shapes with flattened bottoms. However as the dissolution proceeds, terrace adatoms, corresponding approx. to the c unit cell parameter of hydrocerussite, appear near the edges of deeper etch pits (~3 nm, Fig. 1).

Figure 1: Nanoscopic dissolution rate of hydrocerussite

Following the methodology described by Rufe & Hochella [3], an assessment of the nanoscopic dissolution rate of hydrocerussite was obtained (Fig. 1) for the first time in the literature.


The origin of Naxos migmatites: SIMS U-Pb and O isotope analysis of zircon

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The Naxos (Aegean Sea, Greece) structural and thermal dome is cored by migmatites that record the peak P-T conditions (6-8 kbar; ≤700°C) of a late Alpine (18 Ma) Barrovian type metamorphism [1]. The ‘leucogneiss core’ comprises various types of anatectic gneisses thought to derive from either ‘pre-Alpine basement’ or Mesozoic sedimentary protoliths or both. Early Miocene intense deformation and metamorphism has obliterated most prior evidence, leaving zircon as the major tool for unveiling the pre- and early-Alpine history of the Naxos core. SIMS U-Pb dating of zircons from the four major types of gneisses in the core shows that oscillatory zoned domains yield concordia ages of ca. 326, 315, 312 and 300 ± 5 Ma with inherited cores of ca. 500-2500 Ma. Clear overgrowths yield ages between 17 and 20 Ma. Intermediate ages between ca. 300 and 17 Ma are restricted to blurred or porous zircon domains and are aligned on discordia lines connecting these end points. The age data indicate that the protoliths of the migmatites were Variscan igneous intrusions with inheritance of Pan-African and older detritus. Zircons from a pelite raft within the core yield the same age pattern as the migmatites suggesting that these sediments were derived from a similar basement.

SIMS O isotope analysis of oscillatory zoned zircon domains of Variscan age yielded δ18O (Zrn) of 6.5-8.5‰. However in each sample these values vary within a 1‰ range, further supporting the igneous origin of the Naxos migmatites.

Noble gases used as an indicator of groundwater mixing in Azraq, Jordan

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Several sources contribute to the noble gas content in groundwater. One component arises from an equilibrium between soil air and percolating water. Excess air (EA) accounts for an additional noble gas contribution [1]. This applies to all noble gases. Helium has additional sources: 4He is generated by radiogenic production within the aquifer matrix, while 3He originates from tritium decay in young groundwater. A mantle helium component can shift the 3He/4He ratio to higher values. To determine the excess helium component all other noble gases need to be measured in order to separate the excess from the equilibrium and the EA component.

As part of an interdisciplinary research initiative to study water issues in Jordan, we use noble gases to investigate groundwater origin and recharge. In the region of Kerak in Western Jordan, a groundwater recharge estimation project is being conducted, based on tritium-3He dating.

Here a study of groundwater origin in the Azraq Basin in Eastern Jordan, which is affected by groundwater depletion, is presented. The excess of 3He as well as the 3He/4He ratio are used to identify groundwater mixing near the Azraq Oasis. In this area groundwater is used only from the upper aquifer, since the deeper one consists of highly saline water. However, a few production wells in the upper aquifer have shown a rising salt content over the past years. A correlation between the salinity and the 3He excess is detected which argues for an inflow of water from the saline and old aquifer below. In the case of Azraq also the 3He/4He ratio seems to corroborate the above finding, as a 3He/4He vs. Ne/4He isotope plot indicates mantle helium in the saline wells.


Implications of U-Pb-Hf detrital zircon data on the Precambrian crustal evolution of NW India

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We have integrated in situ U-Pb-Hf data for 217 zircon grains from two quartzite samples of NW Indian plate to understand the Precambrian crustal evolution of this region. The U-Pb data unravel prominent probability age peaks at ca. 1.77, 1.85, 2.2, 2.5, 2.7 and 2.9 Ga. Barring 1.77 and 2.2 Ga age peaks, others are correlatable with most of the magmatic events identified in the basement of NW India.

![Figure 1: \( t(Hf) \) versus 207Pb/206Pb diagram showing results of detrital zircons from NW India.](image)

The Lu-Hf isotope analyses indicate that at 1.77 and 1.85 Ga, reworking of Neoarchaean crust dominated over juvenile input as indicated by their largely subchondritic \( t(Hf) \) values. At 2.5 Ga the zircons show a wide scatter in \( t(Hf) \) values but the dominance of subchondritic values also indicate substantial reworking of older crust at this time. On the contrary, during 3.1–2.7 Ga, variable but mostly superchondritic to nearly chondritic \( t(Hf) \) values suggest the dominant production of juvenile crust. The Hf model ages for Neoarchaean zircons also signify that the oldest crust in the NW Indian plate was formed from a depleted mantle source at around 3.8-3.7 Ga.
Impact of ferrihydrite coating and aeration conditions on microbial selenium (Se) reduction and retention in artificial soil aggregates

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Soils display large variations with respect to their physical, geochemical and biological characteristics at scales ranging from nanometers to kilometers. The impact of this heterogeneity on biogeochemical processes is as of yet poorly understood. In structured soils, the aggregate scale (mm-cm) is of particular interest due to the sharp transition in pore size at the surface of aggregates. Small intra-aggregate pores limit advective transport thus facilitating the formation of chemical concentration gradients that promote spatial variation in biogeochemical processes. One such process is the microbial reduction of selenium (Se), both an essential micronutrient and a toxicant. A mechanistic understanding of Se reduction within soil aggregates may lead to improved prediction of its transport and attenuation in soils of contaminated areas.

In order to investigate the coupling of physical and biogeochemical processes controlling Se reduction at the aggregate scale, we used artificial aggregates in flow-through reactor cells, mimicking the interface between soil micropores and macropores. Aggregates were constructed using either uncoated sand or ferrihydrite-coated sand homogenously inoculated with Se-reducing bacteria (*Thauera selenatis* and *Enterobacter cloacae* SLD1a-1 were compared). Saturated flow of aerobic or anaerobic artificial groundwater medium containing selenate and an electron donor, was initiated. Concentrations of selenite and total Se were measured in the outflow solution and in concentric sections of the aggregates' air dried solid phase.

Selenite export rates from aggregates increased by a factor of 600 between aerobic *T. selenatis* reactors with low selenate and acetate input and anaerobic *E. cloacae* reactors with high selenate and pyruvate input. Aerobic input solution significantly decreased Se reduction, however, the presence of a selenite signal indicates the occurrence of anaerobic/microaerobic microzones within aggregates. Solid phase selenite concentrations increased from the exterior to the core under aerobic as well as anaerobic conditions within both sand and ferrihydrite-coated sand aggregates. This is an indication that soil structure can impact Se retention in soils under a diverse set of conditions and that consideration of aggregate scale reactive transport may be essential for a complete understanding of field dynamics.

Metal mobility in clay formations – From batch experiments with mineral suspensions to column setup with compacted clay

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Nowadays, there is a broad consensus on the technical merits of the disposal of high-level nuclear waste (HLW) in deep and stable geological clay formations. For the long-term disposal of radioactive waste, detailed information about geochemical behaviour of radioactive and toxic metal ions under environmental conditions is necessary.

In our project europium, gadolinium (homologues of americium and curium) and uranium were used and their sorption and desorption behaviour onto Opalinus clay was studied [1]. Natural organic matter (NOM) can play an important role in the immobilisation or mobilisation of metal ions due to complexation and colloid formation. This complexation could interfere the sorption of metal ions onto clay. In addition to humic acid (HA) we used other natural appearing organics in Opalinus clay like lactate, formiate or propionate [2]. Therefore, we investigated the complexation behaviour of the metals with NOM as well as the influence of present NOM on the metal sorption onto clay [3].

Capillary electrophoresis hyphenated with inductively coupled plasma mass spectrometry (CE-ICP-MS) has been used to study the complexation behaviour of Eu (III), Gd (III) and U (VI) with HA. The influences of metal concentration as well as the presence of competing cations from clay dissolution as well as cations from clay porewater on the complexation behaviour was analysed [4]. For the sorption/desorption behaviour common batch experiments with mineral suspensions are performed, and in comparison a miniaturised column setup with compressed clay was used to study the influence of NOM on the metal mobility in compact Opalinus clay.

The authors thank the BMWi for financial support (grant no. 02E9683 and 02E10196).

Boron isotope geochemistry of subseafloor hydrothermal ore deposits, Agrokipia B, in Troodos ophiolite, Cyprus

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Cyprus-type ore deposits in many ophiolites are regarded as fossil examples of ore forming processes occurring at modern hydrothermal vent area. Hole CY2A was drilled into stockwork zone of the subseafloor Agrokipia B deposit. Boron is a useful tracer for understanding geochemical mechanism of fluid-related processes because of its chemical properties of high incompatibility and fluid mobility.

Basalts altered at low temperature (Zone A) are relatively enriched in boron (6.2–31.7 ppm) and give the average value of 21.1 ppm. On the other hand, mineralized basalts and dolerites altered at high temperature (Zones B, C, and D) have lower boron contents (0.92–17.0 ppm) and show no trend with stratigraphic depth. The $^{11}$B values of basalts from upper 450 m slightly increase with depth from 2.4 to 4.8‰, whereas those of basalts and dolerites below 450 m show a significant decrease with increasing depth. The lowermost dolerite and sulfide-enriched part of dolerite have as low as $<6$‰ of $^{11}$B.

We conclude that the rocks around Agrokipia B experienced relatively low temperature in recharge zone when Agrokipia A deposits was formed and that high temperature alterations overprinted boron content and isotopic composition of altered rocks to form the subseafloor Agrokipia B deposit. This demonstrates that boron is a good new proxy to analyze and trace hydrothermal alteration and its stages.

Continental materials around the bottom of the mantle transition zone

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Recent progress in our understanding of the consuming plate boundary indicates the ubiquitous occurrence of tectonic erosion of the hanging wall of the continental margin, sediment-trapped subduction, and direct subduction of immature oceanic arcs into deep mantle. Geological studies have estimated the volume of subducted tonalite–trondhjemite–granodiorite (TTG) materials to about seven times the surface total volume of continental crust. To reveal the fate of subducted crusts and how they recycle within the Earth, we studied high-pressure densities and elastic properties of TTG by means of the first principles computation method and compared them to those of peridotite. We found that TTG is gravitationally stable and its seismic velocities are remarkably faster than peridotite in the depth range from 270 to 800 km, especially from 300 to 670 km. We, therefore, propose SiO$_2$-rich second continents around the bottom of the mantle transition zone, which used to form the TTG crust on the Earth’s surface. Our proposed model may provide reasonable explanations of seismological observations such as the splitting of the 670 km discontinuity and seismic scatterers in the uppermost part of the lower mantle. The difference in seismic velocities between PREM model and experimental results in the lower part of the transition zone can be explained by 25 volumetric% of TTG, which would correspond to about several times the present volume of the continental crust. Formation and dynamics of those second continents would have controlled the Earth’s thermal history over geologic time.
Zircon behavior in the upper amphibolite facies polymetamorphic terrane, Ryoke belt, Japan

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In the Ryoke metamorphic belt at the Aoyama area, SW Japan, pelitic schists and migmatites are widely outcropped, and the P-T condition of the regional metamorphism by which they were formed is estimated to be 3.0–4.0kbar, 615–670°C for the Sil-Kfs zone at the north, and 4.5–6.0kbar, 650–800°C for the Grt-Crd zone at the south [1]. The U-Th-Pb dating of the monazite in migmatites yielded 96.5±1.9Ma mainly preserved in the monazite core, and domains and rims of 83.5±2.4Ma. Although the contact metamorphism by the Ao granite at the south (79.8±3.9Ma) was not detected from the major metamorphic minerals, the coincidence of the age suggests that the Younger Ryoke granite including the Ao granite caused the contact metamorphism to the regional metamorphic rocks [2].

In the Grt-Crd zone where metamorphic temperature increases toward the south, zircon grains larger than 20 µm in diameter were abundant in the north than in the south. The comparison between the modal amount of zircon larger than 20µm and the whole-rock Zr concentration suggests that most of the whole-rock Zr was residuated in zircon larger than 20µm in the north, whereas zircon larger than 20µm can account for only 20-30% of the whole-rock Zr in the south. The U-Pb dating of zircon by LA-ICPMS showed that most of the zircon larger than 20µm from the northernmost part of the Grt-Crd zone are detrital in origin. On the other hand, in the pelitic migmatite from the area where metamorphic temperature of 720 °C is estimated, several grains of ~100Ma zircon larger than 20 µm were found.

These observations suggest that upper amphibolite grade metamorphism that potentially lasted about 5Ma [3] is not sufficient enough to (re)crystallize new zircon larger than 20µm, although monazite is almost completely rejuvenated. It is necessary to date tiny-grained zircon less than 20µm, or instead, use monazite in order to date upper amphibolite facies metamorphism.


Increased stable carbon isotopic ratios of oxalic, malonic, and glyoxylic acids in the Arctic aerosols during polar sunrise and after

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Low molecular weight dicarboxylic acids such as oxalic acid (C2) are present abundantly in aerosols. Because they are water-soluble, dicarboxylic acids can enhance the hygroscopic properties of atmospheric particles. During the polar sunrise season at Alert, Canadian Arctic, we observed photochemical production and loss of small dicarboxylic acids [1]. Although C2 is the dominant diacid species in winter to spring, it was replaced by succinic acid after polar sunrise in May. Oxalic acid was preferentially decomposed when a solar radiation was intensified and the atmospheric transport from mid latitudes was ended in May. In this study, we applied compound-specific stable isotope analysis for diacids and related compounds isolated from the Arctic aerosols collected from late winter to early summer including dark winter and polar sunrise seasons.

Stable carbon isotopic ratios (δ13C) of small dicarboxylic acids and ketoacids were measured in the Arctic aerosols after derivatization to butyl esters and/or dibutoxy acetals using a capillary gas chromatography combined to on-line combustion/isotope ratio mass spectrometer [2]. We found that δ13C of C2 increased from -23‰ in early March (before polar sunrise) to -5‰ in May (after polar sunrise). Malonic acid (C3) also showed an increase of δ13C from late February (-25‰) to early May (-17‰). Glyoxylic acid (HOC-CHO), a precursor of C2, showed similar increase from -18‰ in late February to -10‰ in May. Glyoxylic acid (HOC-CHO), another precursor of C2 showed very high isotopic ratios up to +15‰. In contrast, isotopic composition of succinic acid (-32‰ to -24‰) did not show a systematic trend. An increase in δ13C values is probably associated with photochemical ageing of aerosols. It is likely that 12C-13C bonds of oxalic and other species decompose preferentially over 12C-12C bonds during photochemical ageing. Isotopic fractionation of C2 and its precursors may also be likely during the gas/particle portioning. Here, we propose that δ13C of oxalic acid can be used as a photochemical tracer for the ageing of organic aerosols.

Stable isotope approach for feeding structure of mudskipper
Periophthalmus argenteilineatus at different habitats in Okinawa Islands, Japan

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Introduction

Barred mudskipper Periophthalmus argenteilineatus is an amphibious gobiod fish, inhabiting in mudflats, mangroves and port. Mudskippers are known as a carnivorous fish that feed insects as well as benthic animals such as small crustacea on intertidal area [1, 2]. While adult males of the mudskipper have territory around their nests, adult females move along with tidal migration front without their nests. Because the adult individuals have not been observed to move wide range habitats (e.g. between river systems), food differences of barred mudskippers are expected to reflect food availability of each habitat. Stable isotope is one of the powerful tools for studies of food chain in an ecosystem. This study is to reveal food differences attributed to differences of habitat environment and feeding behavior between males and females, using stable isotopic methods.

Materials and Methods

Mudskipper, other benthic animals, particulate matter and sediments were taken from intertidal area of mudflats and mangroves around tropical coral reefs of Okinawa, Japan. Mudskipper samples were separated into gut and muscular tissues. Then, all the organic tissue were freeze-dried and analyzed δ13C, δ15N, δ34S using a continuous flow EA/IRMS (Delta V advantage, Thermo).

Results and Discussion

Muscular tissues of mudskipper showed δ13C = -17.4‰ and δ15N = 7.4‰ at Iriomote Island; δ13C = -21.3‰ and δ15N = 11.8‰ at Okinawa Island. These results suggested significantly different food sources and availabilities of the two islands.


Assessment of cloud droplet growth based on the measurements of hygroscopicity and CCN activity of aerosol particles in Nagoya, Japan

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To better understand the aerosol-cloud relationship in the atmosphere, we investigated hygroscopicity and CCN activity of aerosol particles by ground-based observation, and performed model calculations to predict the concentrations and the effective radii of cloud droplets (Neff and Reff, respectively) formed from the observed particles. The field observation was conducted in the city of Nagoya, from 29 July to 3 August, 2010. The hygroscopic growth of aerosol particles were measured using a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA). The aerosol particles were classified by the dry mobility diameter in the first DMA, and were further classified by the diameter under the condition of 85% relative humidity in the second DMA. A CCN counter (CCNC) and a condensation particle counter to measure CCN and condensation nuclei were connected to the second DMA. The CCN were measured at supersaturations of 0.17%, 0.48%, and 0.93%. The hygroscopic growth factors (HGFs) of studied particles were 1.0, 1.1, 1.25, and 1.4.

The measured CCN activation diameters (dact) were smaller than those predicted; i.e. the actual CCN activity was higher than that predicted. Whereas the differences between predicted and measured dact were not very large for more hygroscopic particles, they were remarkable for particles with HGF of 1.0. Based on the HGF data, we performed model calculations to investigate how the differences of particle hygroscopicity and the differences between predicted and measured dact for particles with HGF of ~1.0 affect the cloud droplet formation. If less hygroscopic aerosol particles in addition to more hygroscopic particles are considered in the cases of large updraft velocity conditions, Na and Reff are, respectively, substantially larger and smaller than those calculated with consideration of only more hygroscopic particles. Further, if we correct the model inputs based on the differences between predicted and measured dact, Na increase and Reff decrease slightly. These results suggest that less hygroscopic aerosol particles in the urban area could contribute to the cloud droplet formation, and play an considerable role in the formation of clouds.
Högbomite from West Ongul Island, Lützow-Holm Complex, East Antarctica

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Högbomite has been found within magnetite megacrysts (5 cm × 3 cm) from the upper amphibolite- to granulite-facies pegmatite cutting the medium-grained quartzo-feldspathic garnet-biotite gneiss at West Ongul Island, Lützow-Holm Complex, East Antarctica. Associated minerals included in magnetite are biotite, plagioclase, hercynite, sillimanite, corundum, quartz, rutile, ilmenite, hematite, and zircon. Högbomite occurs as very fine euhedral to subhedral crystal (5-20 µm) along grain boundaries between magnetite and ilmenite or less commonly enclosed in hercynite (Fig. 1) and in magnetite. Quartz is found in hercynite. Högbomite is in direct contact with hercynite. Ilmenite contains hematite exsolution lamellae. Hematite also forms exsolution lamellae in rutile, which is trapped in ilmenite. Corundum is in direct contact with magnetite, hercynite or sillimanite. Electron microprobe analyses of högbomite yield 2.6-7.9 wt% TiO₂, 60-64 wt% Al₂O₃, 0-0.1 wt% Cr₂O₃, 18-25 wt% Fe (as FeO), 0.3-0.6 wt% MnO, 2.9-4.4 wt% MgO, 4.8-10 wt% ZnO, 0.61-0.01 wt% SnO₂, and 0.20-0.36 X_Mg. Hercynite varies 4.9-14 wt% ZnO and 0.23-0.36 X_Mg. Sillimanite contains 0.6-3.6 wt% Fe₂O₃ from rim to core and < 0.1 wt% TiO₂. Textures and mineral chemistry suggest that the reaction, Mag + Ilm + H₂O + O₂ → Hög + Hc + Qtz, took place at retrograde stage (T < 600 °C) whereby magnetite and ilmenite contained impurities Si, Al, Zn and Mg. Hydrous and oxidized fluid, possibly supplied by crystallization process of pegmatite, were sufficiently enough to form högbomite and biotite. Subsequent cooling processes hematite crystallized as exsolution lamellae from ilmenite and rutile, and sillimanite and corundum became Fe₂O₃-poor at the rim.

Figure 1: Backscattered image of högbomite + hercynite and her-cynite + quartz in magnetite.

Neogene Central Andean adakites, frontal arc migration and forearc subduction erosion at 27°-28.5°S

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Glassy plagioclase phenocryst-free 8 to 2 Ma Andean andesitic lavas erupted at 27°-28.5°S can be argued to contain continental crust incorporated in the sub-arc mantle by forearc erosion as well as by melting in the overlying ~65-70 km thick crust. These distinctive ~7.7 Ma pyx-bearing Dos Hermanos and 7-2 Ma amp-bearing Pircas Negras lavas (54-64% SiO₂) erupted as the frontal arc was being displaced ~50 km eastward over a developing bend in the Wadati-Benioff zone that now marks the Chilean flat-slab northern margin [1]. These lavas can show the most HFSE depletion (La/Ta=40-100) and adakitic-like character (Sm/Yb=4-9; Sr=600-1400 ppm) among Neogene lavas in the region and have higher ⁸⁷Sr/⁸⁶Sr (0.7055-0.7065) than 26-13 Ma lavas (~0.7055). Some 5-3 Ma lavas have high Mg# (to 61), Cr (to 250 ppm) and Ni (to 65 ppm). Their chemistry fits with trace element and isotopic models [2, 3] that begin with > 2 GPa partial melts of ~85:15 mixtures of mafic Jurassic and silicic Paleozoic Chilean forearc rocks reacting with sub-arc mantle peridotite. Mineral thermometry and MELTS program models for the Pircas Negras lavas indicate pre-eruption temperatures near 1050°C showing these magmas can then mix with and melt the overlying eclogitic crust. Given a constant arc-trench gap over the last 8 Ma, ~124 km³/m. y./km of forearc crust needs to be removed to account for frontal arc migration at 8 to 2 Ma and is readily available to contaminate the mantle wedge.

Cathodoluminescence characterization of He⁺ ion implanted plagioclase

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Cathodoluminescence (CL) techniques have been often used as an effective tool to visualize radiation halos in quartz. No investigation of radiation effects on CL of feldspar has been performed to date, although the visible halos can easily be found in the feldspar directly attached to radioactive minerals. In this study, CL of plagioclase implanted by He⁺ ion has been conducted to clarify radiation effect on CL of plagioclase.

Single crystals of albite (Or₁Ab₉₉) from Minas Gerais, Brazil, oligoclase (Or₂Ab₉₂An₁₆) from Inabu, Japan, andesine (Or₁Ab₅₃An₄₆) from Bekily, Madagascar; and anorthite (Ab₅An₉₅) from Yoichi, Japan were selected for CL measurements. He⁺ ion implantation with 4.0 MeV (dose density: 2.18 × 10¹⁶ to 6.33 × 10¹⁸ C/cm²) on the samples was conducted using a 3M-tandem ion accelerator at the Takasaki Research Center of the Japan Atomic Energy Research Institute.

CL spectra of unimplanted and implanted plagioclase show emission bands at 350, 420, 580 and 740 nm. Implanted albite and oligoclase exhibit characteristic red emissions at 700–750 nm, where the intensities increase with an increase in radiation dose. Spectral deconvolution of albite and oligoclase samples can successfully separate the red emission into three Gaussian components at 1.861, 1.644, and 1.557 eV. Integral intensity of the component at 1.86 eV linearly correlates with radiation dose. The CL spectra of andesine and anorthite show no component at 1.861 eV. The component at 1.861 eV might be attributed to oxygen vacancy between Al and Si tetrahedra associated with two Na atoms (O³⁺/₂Al × 2²Na center). The component intensity clearly correlates with radiation dose as a function of O³⁺/₂Al × 2²Na center, but does not depend on the concentration and distribution of other emission centers, degree of Si-Al order and presence of microstructures or texture. CL spectral deconvolution, therefore, may be applied to evaluate radiation dose of alpha particles from natural radionuclides on Na-rich feldspar.

Semi detail orientation survey in semi arid conditions and mineral influenced basin, case study in Southestern Iran

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Semi Detail orientation survey

The aim of this research is to find the optimum size fraction of stream sediment sampling in semi detail geochemical sampling and mineral influenced basin. In this study 21 stream sediment samples collected from of streams that draining Cu-Mo porphyry deposits in southeast of Iran.

Discussion of Results

The charts (e.g. Fig. 1) suggest that >500 µm fractions give the strongest and most consistent anomalies for Cu, Mo and Au while 500-250 µm fractions give better Zn and Pb anomalies. The finer size fractions give a stronger anomaly response for gold [12]. By sampling the fine sediment fractions with high sampling density, uncertainty associated with the nuggety nature of gold can be reduced to a level [1]. In detail stream geochemistry the anomaly are not affected by Aeolian dust deposits respectively.

Testing the ‘post-glacial weathering peak’ hypothesis – A lacustrine record of $^{87}$Sr/$^{86}$Sr

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Chemical weathering of the continents regulates levels of atmospheric CO2, thereby acting as a primary control on Earth’s climate [1]. The effect of continental ice sheets, as observed during the Pleistocene, on this regulation of global climate is not clear. It has been suggested that repeated transitions between glacial (high physical weathering) and interglacial (high chemical weathering) states may have enhanced CO2 drawdown during the Quaternary [2].

[2] argue that present riverine inputs to the oceans are still distorted by the last glaciation and are above the long-term average. During the incipient stages of chemical weathering the Sr released is more radiogenic than the bulk rock [3, 4]. Therefore, associated with the landscape rejuvenation caused by each Pleistocene glaciation one might expect a peak in radiogenic Sr in continental runoff. Such a ‘post-glacial weathering peak’ is required to explain the modern marine Sr isotope composition from ~40ka (1996). Preliminary data from ostracods in previously studied sediment cores from Owens Lake, California (e.g. [6]).

We attempt to test the ‘weathering peak’ hypothesis by constructing a record of Sr isotope composition of waters draining the Sierra Nevada through the last glaciation using ostracods in previously studied sediment cores from Owens Lake, California (e.g. [6]). Preliminary data from ostracods in Holocene sediments show elevated $^{87}$Sr/$^{86}$Sr relative to the modern flow-weighted mean $^{86}$Sr/$^{86}$Sr of streams in the Owens Lake drainage (0.70911) [7]. Further analyses will complete a record of the Owens Lake Sr isotope composition from ~40ka to the present day and will allow for a comparison to the contemporaneous extent of glaciers in the Sierra Nevada [6] thus allowing us to test the ‘post-glacial weathering peak’ hypothesis.


As, Fe and S cycling during reductive biomineralisation of pedogenic jarosite


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Jarosite (KFe3(SO4)2(OH)6) is an abundant Fe (III) mineral phase and important contaminant sorbent in coastal acid sulfate soils (ASS) [1]. Jarosite in these environments can be prone to reductive dissolution as a result of changes in local hydrology (e.g. sea-level rise and tidal seawater reflooding) [2]. However, very few studies have examined the reductive dissolution and transformation of K-jarosite, and the associated effects on contaminant mobility following seawater inundation of a jarosite-rich soil. Here we investigate the reductive biomineralisation of a natural As (V)-bearing pedogenic K-jarosite and explore the effects of a seawater gradient on the cycling of As, Fe and S. Solid and aqueous phase partitioning and speciation of As, Fe and S were determined using a wide variety of techniques including As- and S- K-edge XAS, TEM-SEM, SEM and XRD.

Whilst the rate and magnitude of fermentation processes were initially similar across the seawater gradient (100%, 10%, 1%), reductive dissolution of jarosite proceeded faster under 100% seawater conditions. Concentrations of Fe$^{2+}$ were ~4-fold higher in 100% seawater and Fe$^{2+}$/K$^{+}$ ratios were initially congruent with respect to solid-phase jarosite. Evidence suggests both dissimilatory reduction of jarosite-Fe (III) and abiotic reduction of Fe (III) by sulfide produced via sulfate-reducing bacteria. Residual jarosite became increasingly polycrystalline and developed hollow cores. Disordered nano-particle mackinawite was a primary mineralisation product after 140 days in 100% seawater.

While As mobilisation was generally correlated with Fe$^{2+}$ production, As displayed highly contrasting kinetics across the seawater gradient. Initial release of As$^{3+}$ was most rapid in low seawater treatments. Although As mobilisation in 100% seawater eventually exceeded the low seawater treatments, it was not substantially attenuated by the formation of mackinawite. The proportion of solid-phase As (III) increased over time and was greatest in 100% seawater. Findings provide important insights into the reductive dissolution of pedogenic jarosite following seawater inundation in coastal ASS environments.

On the significance of ultra-magnesian olivines in basaltic rocks

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The temperature regime in the Earth’s mantle is of prime importance for models of mantle convection and a key test of the mantle plume hypothesis. Olivine thermometry is commonly used to constrain mantle potential temperatures in basaltic magmatic provinces. Ultra-magnesian olivines, here defined as Fo > 92, are common in Archean komatiites and occasionally observed in Phanerozoic LIPs. The presence of ultra-magnesian olivines is generally interpreted as evidence for melts with extremely high MgO concentration and high eruption temperatures. Such melts are considered to be a hallmark of a hotter mantle in the early Earth and of thermal anomalies related to Phanerozoic mantle plumes. Estimating primary melt compositions and temperature based on mineral and rock data is a common approach but subject to large uncertainties. A better alternative is direct study of melt inclusions trapped in ultra-magnesian olivines. These inclusions are interpreted to have been feeders to the Etendeka volcanics and are characterized by the local presence of high MgO (picritic) compositions. The composition of melt inclusions trapped in ultra-magnesian olivine (Fo100) from the HOD contradicts the predicted 24 wt. % MgO for parental melts and 1680 °C mantle potential temperature indicated by these compositions is 1520 °C. Most olivines in the HOD rocks with Fo > 85 are too Mg-rich to be in equilibrium with the whole-rock composition, indicating that the grains are entrained xenocrysts from earlier, more magnesian melts. We show that ultra-magnesian olivines can be produced by protracted melt extraction from the mantle source and that this process also leaves a distinctive depletion in the incompatible trace elements.


A poor man’s enzyme? Effects of reactive Mn(III)-oxalate complexes on structurally intact plant cell walls

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Manganese (III)-ligand complexes such as Mn (III)-oxalate are potent and highly diffusible oxidizers for lignin model compounds [1, 2]. Although there is clear indication for their potential role in lignin decomposition processes in soils [3, 4], few reports exist on mechanistic aspects such as substrate specificity, reaction kinetics and oxidizing power of Mn (III)-oxalate complexes reacting with structurally intact plant materials. This is of particular importance in the context of soil organic matter decomposition since lignin cannot be viewed as a single substance [5], but has to be seen as an integral component of ligno-carbohydrate complexes (LCC) in fresh plant cell walls (e.g. in litter, root and wood).

Here we tested the hypothesis that Mn (III)-oxalate complexes may act as a 'pretreatment' for structurally intact LCC components in plant cell walls. The diffusible oxidizers are thought to be small enough to penetrate and react with composite LCC in cell walls, thereby increasing porosity which permits access to more efficient lignin- and cellulose-decomposing enzymes. This was investigated by reacting cell walls of single Zinnia elegans tracheary elements with Mn (III)-oxalate complexes in a continuous flow-through micro-reactor. The uniformity of these individual plant cells allowed us to examine Mn (III)-induced changes in cell wall chemistry and ultrastructure on the micro-scale using fluorescence and electron microscopy as well as IR and X-ray spectromicroscopy. This presentation will discuss the specificity of Mn (III)-complexes for certain cell wall functionalities, the impact of such reactions on cell integrity, and potential implications for soil C cycling.

The influence of co-contaminant complexing agents on radionuclide environmental behaviour

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Organic complexing agents that are co-disposed in radioactive waste or formed \textit{in situ} may enhance the migration of radionuclides at contaminated sites. However, the mechanisms of the interactions are poorly understood. We have therefore undertaken an extensive program of research to probe the speciation of radionuclide-organic co-contaminant complexes, competitive interactions with common metal ions and the mechanisms by which the complexing agents impact radionuclide sorption and transport. This work has utilised electrospray ionisation mass spectrometry for the characterisation of aqueous speciation, kinetic batch sorption experiments using a relevant, characterised terrestrial sand (Drigg sand) and dynamic column experiments coupled with the k1D transport code. Thorium (IV), U (VI), Sr (II) and Cs (I) were selected as model radionuclides of different oxidation states and EDTA, NTA, picolinic acid and isosaccharinic acid were included as key complexing agents.

The complexing agents generally influenced radionuclide behaviour in the expected order of Th>U (VI)>Sr, with no discernable effect on Cs, and EDTA generally exerted the greatest influence of the complexing agents. However, the results highlighted the complexity of these interactions. In several cases, the speciation of the complexes was more diverse than suggested by the existing speciation databases. Also, the kinetics of exchange between radionuclide complexes and common metal ions varied from occurring virtually instantaneously to over several months, and could involve precipitated metal phases.

Batch experiments demonstrated that the concentration of the radionuclide strongly influences the effect that a complexing agent can have, in terms of both the kinetics of sorption and the equilibrium position. Finally, transport experiments identified that the formation of ThEDTA complexes enhances Th transport, but that at higher Th concentrations, EDTA-mediated colloidal Th transport occurs. The key data from these studies will be presented and discussed in terms of the environmental importance of the complexing agents.

Geochemical study and U/Th dating of the Akköy fissure ridge travertine (SW-Turkey): Paleoclimatic and paleoseismic interpretations

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Fissure ridge travertines are elongated, wedge-like nonmarine carbonate deposits formed due to CO\textsubscript{2} degassing from carbonate rich thermal spring waters. They are well-known indicators of past and present seismic activity, including Quaternary and prehistoric major earthquake events, as generally deposited from springs discharging in co-seismic extensional fissures along major active faults \cite{1, 2}. The precipitation of travertines is strongly influenced by the water supply controlled mainly by climate, thus the question must be raised, whether the tectonic and/or climatic processes has the major role on their deposition.

To answer the question, we performed detailed U-series dating and stable isotope and trace elemental study of travertines collected along a vertical section, through the bedded layers of the Akköy, Karakaya Hill fissure ridge (Denizli Basin, SW-Turkey). The U-series age data range from 45±108 ka to 18±0.3 ka. The more or less continuous travertine deposition at the Akköy fissure ridge during cold-dry and warm-wet climatic events indicates that the travertine deposition was controlled strongly by tectonic processes, i.e. the area of the Denizli Basin was seismically active during the period mentioned above. The trace element concentrations of the bedded travertine deposits show temporal change in the geochemistry of the travertine depositing thermal water.

\cite{1} Hancock \textit{et al.} (1999) \textit{J. Struct. Geol.} \textbf{21}, 903–916.
Mantle melting and melt transport beneath oceanic spreading ridges

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Degree of melting & potential temperature

Reactions of cooling melt with shallow peridotite can reset indicators of degree of melting and potential temperature in both melt and residual peridotite. Yb concentration and spinel Cr# in peridotite are affected by (a) small scale variations in reactive melt transport, (b) variable extents of melt extraction, and (c) ‘impregnation’, i.e. partial crystallization of cooling melt in pore space. Also, many peridotites at ridges may have undergone several extensive partial melting events over Earth history, while others could be residues of extensive melt extraction from mafic heterogeneities in the mantle source.

Melt focusing to ridges

Modeled crystallization of cooling melt in the shallow mantle can create a permeability barrier guiding underlying melt diagonally toward the ridge, but field studies have not identified such barriers. Permeable ‘shear bands’ may guide melt to the ridge, but the nature of shear bands in open systems at natural grain size and strain rates is uncertain. 2D and 3D focused solid upwelling due to melt buoyancy and weakening as a function of permeability – especially increasing permeability with decreasing pyroxene content during melting – may warrant more attention.

Crustal thickness, spreading rate & melt productivity

The following three statements are inconsistent: (1) Modeled peridotite melt productivity beyond cpx exhaustion is ≥ 0.11%/GPa. (2) Crustal thickness is independent of spreading rate. (3) Thermal models predict, and observations confirm, thick thermal boundary layers beneath slow spreading ridges. Most sampled peridotites from ridges melted beyond cpx-out. Cpx in these rocks formed via impregnation and/or exsolution during cooling. The data can be understood if (a) melt productivity is << 0.1%/GPa beyond cpx-out, and (b) cpx-out occurs > 15 km below the seafloor beneath most ridges.

Conduit generation and geometry

Dunites, formed by pyroxene dissolution in olivine-saturated melt ascending by porous flow, are conduits for focused porous flow of melt, preserving disequilibrium between melt and pyroxene in surrounding peridotite at P < 1.5 GPa. Perturbations in permeability grow into dunite conduits because incongruent dissolution increases porosity and permeability. Perturbations may arise from ‘shear bands’ and/or heterogeneities in the mantle source. Conduits may also involve mechanical instabilities, if it is easier to open a pore than to close it. Most models and experiments do not produce the power law distribution of dunites at a given depth observed in peridotites, except for some shear band experiments.

Underplating of felsic rocks in arcs

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Buoyant, felsic material may be subducted and then returned to the base of evolving crust via (a) relamination, (b) diapirs in the mantle wedge, and/or (c) imbrication (e.g. [1-5]). Subducting crust is carried to conditions (~700°C and P > 1 to 2 GPa) where garnet is stable, rendering some lithologies denser than mantle peridotite at the same PT, and where material is hot enough to flow viscously in response to buoyancy forces [6]. Whereas delamination and foundering can only remove dense lithologies from a narrow, high PT horizon at the base of typical crust, the entire subducting crustal section can undergo density sorting in subduction zones. Such efficient density sorting may explain why lower continental crustal compositions, including mafic estimates [7], are less dense than peridotite at the same PT [5, 6, 8].

Sediment subduction and ‘subduction erosion’ involve intermediate to felsic shale and greywacke. If they are in layers or blobs with dimensions > 100 m, they will rise buoyantly at > 700-800°C in times < 1 Myr [4]. Inset in a ‘subduction channel’ involves isothermal decompression to a level of neutral buoyancy (a). Most UHP terrains record re-equilibration at 700°C and 0.5-1 GPa, in accord with this idea [5]. Diapirc ascent through the hot mantle wedge (b) will induce extensive melting, producing the ‘sediment component’ in arc magmas [4]. Some trench sediments may be thrust directly into arc lower crust (c), producing andesitic paragneiss recording typical arc Moho PT (~800°C, 1 GPa) [9], as in the North Cascades. Indeed, the 35 km of crust beneath such exposures may itself have been added later, via continued underplating of buoyant, felsic material. In general, arc magma flux estimates that assume subduction erosion always removes arc crust are overestimates.

Arc-arc or continental collision will also lead to efficient separation of dense, mafic rocks from buoyant, felsic metasediments and plutons that rise to neutral buoyancy [5].

As a result, much of the continental lower crust may be quite felsic, similar to typical granulite terrains. This is consistent with Vp and heat flow data provided that some U, Th and K are extracted via decompression melting [5].


Mineralogical Magazine www.minersoc.org
Geochemical and ecological models of plant-driven chemical weathering: Insights into the sinks for atmospheric CO2

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It is generally agreed that rhizospheric acidification of the shallow subsurface – the vascular-plant ‘acid pump’ – accelerates weathering and the loading of soil and drainage waters with base cations, thereby also promoting drainage losses of weathering products (chemical denudation) and lowering atmospheric CO2 levels on geologic timescales [e.g. 1, 2]. Mass-balance tests of this model, in comparative studies of watersheds with different plant covers, report scattered results.

In our experimental mesocosm studies employing the same approach, a single ecosystem exhibits order-of-magnitude variations in chemical weathering and denudation rates over decadal timescales. Our results also show that the silicate-derived Ca+Mg denudation flux, i.e. the lithospheric CO2 sink, is not equivalent to the alkalinity flux, i.e. the hydroospheric sink, because of disturbance-driven strong-acid generation. These results underline the idea that the efficacy of the plant-driven lithospheric CO2 sink, and perhaps associated long-term climate control, may depend on the planet’s geophysical, biological and ecological disturbance regime. It is true that the weathering power of vascular plant systems dwarfs that of nonvascular systems; but the vascular systems also have correspondingly great capacity to conserve the nutrients generated by weathering, by localizing water and nutrient cycles both during growth and following perturbations.

Our findings are consistent with an ecological model in which mechanisms of biologically mediated weathering are adaptive functions of ecosystem state. In this paradigm, which emphasizes the plant as chemical sink and builder of soil and ecosystem nutrient capital, vascular systems are likely to deploy varying portfolios of weathering and nutrient uptake strategies, involving a range of plant physiologies, rhizospheric symbioses, and mass transfer and transport mechanisms with a range of geologic consequences.


Beyond the closure temperature concept: when does 40Ar/39Ar dating constrain exhumation?

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40Ar/39Ar ages determined on metamorphic minerals are commonly assumed to reflect cooling and exhumation, but recently reported experimental results on muscovite suggest a significant pressure dependence of argon diffusion in muscovite, which acts to decrease argon diffusion rates at high pressure. Using numerical diffusion models, which include a pressure correction, we systematically interrogate the assumptions associated with 40Ar/39Ar dating of muscovite in such rocks. We show the pressure-temperature regions in which 40Ar/39Ar dating could constrain the timing of exhumation in an open system, and suggest a method for checking that the rock being dated has behaved as an open system during exhumation. The link between apparent 40Ar/39Ar age and traditional ‘closure temperature’ is shown to be valid only when muscovite crystallized under, or subsequently reached, high temperature and relatively low pressure conditions. Our modelling data suggest that HP and UHP rocks, particularly those that have experienced short orogenic cycles are unlikely to yield cooling and exhumation ages. The results and discussion presented here for muscovite are equally applicable to other metamorphic minerals commonly dated using the 40Ar/39Ar system.
**Si isotope fractionation in high-temperature metal-silicate systems: Implications for core formation**

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The observed difference in Si isotopic composition between CI chondrites and bulk silicate Earth has been explained by high P-T metal-silicate Si isotope fractionation accompanying Si incorporation into Earth’s core [1, 2, 3].

We have measured Si isotopes in metal alloys and co-existing silicate slags that were produced at temperatures of ~1600°C in reducing atmospheric conditions in an industrial blast furnace at Tata Steel IJmuiden, the Netherlands.

Silicon isotopes were measured with a ThermoFinnigan Neptune MC-ICPMS [3] using a modified sample digestion procedure [3, 4]. Our results show an average mass difference of 0.75 ‰ for $^{30}\text{Si}$ between metals and silicates (Fig. 1).

**First episode of widespread ocean oxygenation 551 Myr ago**


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Increasing ocean oxygenation may have spurred the evolution of large multicellular metazoans during the Ediacaran Period (635-542 Myr ago). Fe speciation and other geochemical data from sedimentary rocks indicate that regional ventilation of the deep oceans commenced no later than 580 Myr ago but parts of the Ediacaran deep ocean remained anoxic. Reconstructing the timeline of ocean oxygenation is critical to understanding metazoan evolution, but the spatiotemporal distribution of dissolved O₂ remains poorly understood. In contrast, the Mo isotope composition of euxinic (anoxic/sulphidic) black shales represents a proxy for global seawater and constrains global ocean redox conditions.

Here, we present Mo isotope evidence for the first known episode of widespread ocean oxygenation 551 Myr ago. High-resolution profiles through black shales at the top of the Doushantuo Formation (South China) reveal a transient excursion to heavy $^{98}\text{Mo}$ (from ~0‰ to 2‰) that approaches modern global seawater (2.3‰). The latter has heavy $^{98}\text{Mo}$ largely because isotopically light Mo is preferentially removed into oxic Fe-Mn crusts. We infer a similar extent of Mo burial in oxic sediments 551 Myr ago.

Older euxinic shales deposited between 1840 and 551 Myr ago are enriched in isotopically light Mo and indicate expanded deep ocean anoxia, including a prevalence of euxinic conditions at mid-depths along ocean margins. Between 551 and 400 Myr ago, the Mo isotope database points to an intermediate extent of oxygenation relative to older and younger oceans. We propose that there was a major increase in ocean oxygenation 551 Myr ago which sparked a major diversification of complex macroscopic metazoans.

**Figure 1:** Three isotope plot showing Si isotope data of metals and silicates along the equilibrium fractionation line of Si.

Sign and magnitude of our results are in good agreement with results of high-pressure experiments [3] and theoretical predictions [1]. Si isotope fractionation clearly occurs in high-temperature metal-silicate systems under reducing atmospheric conditions, and high pressures are not required. Our data show that Si could have been incorporated into Earth’s core during its early formation stages.

Halogenes (Cl, Br, I) in basalt glasses

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Halogenes have highly variable concentrations in basalt glass with part of the variation related to mantle abundance. Serpentinites (hydrated mantle lithosphere) are major reservoirs for halogenes in subducting slabs and previous work has shown Br/Cl and I/Cl are strongly fractionated during serpentine breakdown. As a result, fractionated and characteristic low Br/Cl and I/Cl ratios could be useful for tracing the presence of subducted halogenes (and other volatiles) in basalts from different tectonic settings.

The halogen partition coefficients were investigated using a suite of Enriched Mid-Ocean Ridge Basalt glasses from Macquarie Island (70-1400 ppm Cl; MgO of 5.5-9 wt %; La/Sm of 1.4-7.9; typical MORB 3He/4He of ~8 Ra). Log-log covariation diagrams demonstrate Cl, Br, K and U have statistically indistinguishable partition coefficients similar to that of I. Therefore, Br/Cl, I/Cl, K/Cl and U/Cl ratios could be used for tracing the presence of subducted halogenes (and other volatiles) in basalts from different tectonic settings.

The Macquarie MORB mantle has Br/Cl and I/Cl weight ratios of (3.7 ± 0.5) × 10^-3 and (130 ± 100) × 10^-6, respectively. Together with the Cl/K/U data, these ratios suggest 19 ± 6 ppm Cl, 67 ± 31 ppb Br and 7 ± 5 ppb I (24) in the bulk silicate Earth.

Preliminary data for Back-Arc Basin Basalt glasses from Lau and Manus have up to 3000 ppm Cl and variable Br/Cl and I/Cl signatures, including some of the lowest Br/Cl ratios obtained in this study. These data could be partly explained by a Cl contribution from serpentinite breakdown fluids, but data are now required to determine the subduction potential of Br and I in organic-rich meta-sediments.

Possible Platinum Group Element (PGE) clusters in magmatic systems; Using synthetic sulphide melts

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The aim of the study is to verify whether or not the primary binding mechanism of PGE, in a magmatic environment, is a pure chemical or physical/mechanical process. The monosulphide (mss) phases of temperature controlled synthetic melts were investigated for the existence of small Pt clusters or nano-structures (10-100 atoms). If such entities are found, they would point towards an initial physical mechanism as the dominant process during early magma differentiation.

Experiments were run with variable concentrations of Pt, As, Cu, S and Fe, chosen to mimic a natural Cu-Ni-S ± PGE system. Samples were cooled down rapidly (from 1050-25°C in a few seconds) and slowly (1050-400 °C over 48 hours).

Pt forms large heterogeneous distributed Pt-Asx and Pt-Fe phases in 50-50 µm (i.e. approximately 700-166666 atoms). Together with the Cl/K/U data, these ratios suggest 19 ± 6 ppm Cl, 67 ± 31 ppb Br and 7 ± 5 ppb I (24) in the bulk silicate Earth.

Preliminary data for Back-Arc Basin Basalt glasses from Lau and Manus have up to 3000 ppm Cl and variable Br/Cl and I/Cl signatures, including some of the lowest Br/Cl ratios obtained in this study. These data could be partly explained by a Cl contribution from serpentinite breakdown fluids, but data are now required to determine the subduction potential of Br and I in organic-rich meta-sediments.

Oceanic Island Basalts from the Society and Pitcairn seamounts (3He/4He of 1-10 Ra ± solar Ne indicate mixed recycled and primitive components) are characterised by MORB-like I/Cl and Br/Cl ratios. In contrast, low Br/Cl values are expected in dehydrated serpentinites and high I/Cl values are expected in subducted sediments. Therefore, halogenes in basalts with ‘EM-type’ signatures do not carry an obvious recycled signature, but could be explained by mixing recycled, ‘primitive (?)’ and MORB mantle components.
Terrestrialization of the Earth and its influence on the advent of complex life

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For the first 3 billion years of life’s history on Earth single celled organisms were Earth’s sole residents. In the Late Precambrian this record changed dramatically with the appearance of complex multicellular life (metazoans) that rapidly diversified and radiated. This radiation was likely triggered by planetary changes, though what those changes were, how they interacted with intrinsic (genetic) influence and which changes were causes and which effects constitute principal questions in geobiology with important implications for the conditions on other planets necessary to support complex life. Much of what we know of this transformation comes from the marine record because of a strong preservational bias relative to terrestrial sediments. It is evident from studies of the modern biosphere, however, that the terrestrial realm has a critical influence on the sustainability of complex life. While it is widely accepted that the early terrestrial surface of the Earth was inhospitable to life, and the timing of the greening of the Earth’s surface remains poorly constrained, the influence of vascular land plants beginning in the Silurian is commonly believed to have been an important step in establishing the present Earth system. However an earlier more cryptic and simple biomass likely colonized and expanded across the Precambrian landscape, modifying physical and chemical weathering patterns, soil clay mineral production, marine and terrestrial carbon burial, nutrient flux to marine systems and the hydrological cycle. It is reasonable to hypothesize that biogeochemical systems, like clay mineral associated organic carbon preservation and burial, that play an important role in CO₂ sequestration and atmospheric oxygen production today, were initiated during this earlier transition. Secular changes in clay mineral composition of sediments through late Precambrian continental margin sediments show a distinct rise in phyllosilicates in support of this hypothesis. Alteration of the carbon isotopic composition of coastal carbonates by dissolved organic mater in meteoric waters also becomes a pronounced influence during this period of time, and finally new fossil discoveries also point to the terrestrial surface as being an important component in planetary transformation.

A continental amplifier for marine carbon sequestration in a greenhouse ocean

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Recent evidence has increased concern that future climate will be influenced by natural processes and feedbacks more common to a warm climate mode. It is well known from past greenhouse periods that anomalous concentrations of organic carbon were associated with disruption of marine ecosystems, widespread anoxia, and climate perturbations. While most models of black shale formation focus on oceanographic controls, findings on modern continental margin sediments also identify a strong landward influence on marine carbon burial that is also consistent with current understanding of hypoxic zone expansion. Here we show evidence for a direct land-sea mechanism that translates the effects of changing continental climate to carbon burial in deep marine sediments via the preservative effects of detrital clay mineral surfaces. We show a correlation ($r^2=0.75$) at cm resolution between mineral surface area (MSA) and abrupt (centennial or less) high magnitude shifts in TOC from 1% to 15% in pelagic sediments from the tropical Cretaceous Atlantic (ODP 959). Carbon burial was maximized by an enhanced flux of high MSA clay minerals formed in response to increased seasonality in tropical Africa that were exported to hypoxic shelf waters with high dissolved organic carbon concentration. Not only do these data identify a dominating terrestrial influence for back shale formation during one of the ‘Cretaceous Oceanic Anoxic Events’ ~ 85 ma (OAE3), but show that climate under greenhouse conditions can cross a threshold into a highly sensitive mode in which organic carbon burial efficiency is amplified, providing a negative feedback to pCO₂.
Geochemistry of fluids from the Bruce nuclear site: Evidence for a geologically ancient Ordovician porewater system

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Groundwater and porewater geochemistry data were collected at the Bruce nuclear site near Tiverton, ON, located on the northeastern margin of the Michigan Basin, as part of multi-disciplinary site characterization activities for the proposed development of a deep geologic repository (DGR) for low- and intermediate-level radioactive waste (L&ILW).

The site-specific geochemical data is consistent with regional data collected in various locations within the Michigan Basin, suggesting that the origin and evolution of the brines at the regional- and site-scales have been controlled by the same, or similar, processes. The natural tracer data ($\delta^{18}O$, $\delta^2H$, Cl, Br) collected at the Bruce nuclear site support the long-standing hypothesis that the sedimentary brines originated from seawater, or evaporated seawater (e.g. [1, 2]), and have been modified over hundreds of millions of years by various mixing and in situ water-rock interaction processes (e.g. dilution, halite dissolution, dolomitization). In addition, enriched $^{87}$Sr/$^{86}$Sr isotopic signatures throughout the entire Ordovician sedimentary sequence suggest that solute residence times within the Ordovician brines are long and these values are consistent with regional observations (e.g. [3]).

Horizontal hydraulic conductivities ($K_h$) and matrix permeabilities were measured in the Ordovician formations and range between $10^{-15}$ and $10^{-12}$ m/s, and $10^{-20}$ to $10^{-15}$ m$^2$, respectively. Vertical hydraulic conductivities are estimated to be less than $K_{hi}$ by a factor of at least ten in the Ordovician formations, and the presence of high isotopic gradients in the methane and helium compositions ($\delta^{13}C_{CH_4}$, $\delta^2H_{CH_4}$, and $^3$He/$^4$He) indicate that a barrier to vertical solute transport may exist at the base of the Cobourg Formation at the Bruce nuclear site. The geochemistry, when partnered with the physical data, suggests that the Ordovician porewater system is geologically ancient.


Characterising the Earth: Exploiting seismology and mineral physics

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The dominant gradient in Earth properties is radial and this has enabled simple 1-D models to have considerable utility. Seismological reference models have been employed in ways that were not envisaged when they were created. In particular, the parameterizations were chosen for mathematical convenience rather than linked to any particular physical conditions. It should therefore come as no surprise that such seismological models do not conform to the properties expected for mineral physics predictions for reasonable mineral assemblage models and near adiabatic conditions. There will also be biases associated with lateral heterogeneity, e.g. the properties corresponding to the average temperature are not the same as the average of the same properties. Nevertheless seismology provides key tie points through well constrained discontinuities that can calibrate pressure scales, and mineral physics can investigate perfect aggregates and so explore a broad range of likely conditions. Rather than test a particular mineral physics configuration against a specific seismic reference model or a subset of seismological observations, we need to build new physical comparator models that recognise the limitations of both seismic and mineral physics models and provide explicit uncertainties on physical parameters. Such models should work with the standard seismological data sets and recognise the geodynamic state - non-adiabaticity is likely in a convecting system. We can examine the physical state implied by seismic tomography in terms of the predictions for different classes of parameter models and so gain insight into the controls we have on the Earth system.
**Comparing the surface-promoted hydrolysis of phosphate mono- and diesters on goethite**

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Phosphorus is an essential nutrient for both plants and microorganisms. However, in order for it to cross cell membranes, it must be in the form of orthophosphate or in some cases as small organophosphates. The majority of organic phosphates input into the biosphere are in the diester form, via pesticides, plasticizers, and hydraulic fluids. However, the P found in most soils is dominated by monoesters. Hydrolysis of phosphate esters in biological systems is important since it is a step that is required to make these large phosphate esters more bioavailable. While the hydrolysis of these phosphate esters is thermodynamically favourable, the reaction in water or a strong electrolyte solution is a slow process.

Phosphorus is a unique essential nutrient in its ability to strongly sorb to environmental particles. Therefore, reactions at the surfaces of these particles can control the fate and transport of phosphorus in the biosphere. Minerals, such as goethite, have been shown to increase the rate of hydrolysis of organophosphates by acting as a catalyst. In this study we have investigated the abiotic hydrolysis of a phosphate monoester and diester, p-nitrophenyl phosphate (pNPP) and Bis-[p-nitrophenyl] phosphate (BNPP), respectively. To determine the mechanisms and rate of the hydrolysis of pNPP and BNPP adsorbed on goethite surfaces we have used a combination of spectroscopic methods. The concentration of phosphate remaining in solution was determined by UV-vis spectroscopy, while the surface reactions were examined using infrared spectroscopy via the ATR sampling technique.

Spectroscopic results for the pNPP-goethite system show quick and complete adsorption of the ligand, followed by the subsequent hydrolysis, with the release of nitrophenol (NP) into solution. After 30 hours nearly 100% of the pNPP was hydrolyzed to NP and orthophosphate. Alternately, in the BNPP-goethite system, the ligand adsorbs much more slowly and to a lesser extent than the pNPP. Between pH 4 and 6, the maximum hydrolysis observed over 48 hours is less than 25%. Our results suggest that differences in surface affinity and surface-promoted hydrolysis between mono- and diesters are important factors to consider in order to explain differences in the overall biogeochemical behaviour of these two classes of phosphorus compounds.

**Water in the mantle, melting, and the evolution of Earths atmosphere**

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Water and carbon are the most important volatiles in Earth’s interior, but they strongly differ in their behaviour. While carbon is mostly sequestered in accessory phases such as carbonates and elemental carbon, water mostly resides as OH point defects in the nominally anhydrous minerals of the mantle. In this presentation, I review (1) the observational constraints on water abundance in the mantle (2) the effect of water on mantle melting and the associated changes in electrical conductivity and (3) the coupling between the water abundance in Earth’s mantle and the redox evolution of the atmosphere.

Water may be essential for inducing melting in the seismic low velocity zone of the upper mantle as well as above the 410 km discontinuity. Both effects are ultimately related to depth-dependent changes in the capability of mantle minerals to dissolve water as point defects. Major experimental advances in recent years have shown that both the solubility of water in olivine at the base of the upper mantle as well as the solubility of water in pyroxenes in the uppermost mantle are much higher than previously thought. Moreover, new in situ measurements show that water has a much stronger effect in enhancing the electrical conductivity of basaltic melts than anticipated and this effect increases with pressure. A consequence of these observations is that very likely, small fractions of hydrous melt can explain the electrical conductivity in the seismic low velocity zone of the upper mantle.

It has long been recognized that Earth’s atmosphere became much more oxidized in the ‘great oxidation event’ 2.3 billion years ago. This event may be due to a change in oxidation state of volcanic gases or to photosynthesis by cyanobacteria. Changes in the oxidation state of volcanic gases 2.3 billion years ago have often been dismissed on the ground that there is no evidence for a corresponding change in mantle redox state at this time interval. However, the relevant gas equilibria between sulfur and nitrogen species do not only depend on oxygen fugacity, but also on water. I show that degassing of water from the mantle – at constant oxygen fugacity – may well induce the changes in the oxidation state of sulfur and nitrogen in volcanic gases required to oxidize the atmosphere.
Atomistic simulations of uranium in the environment: Diffusion, adsorption, and incorporation

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Uranium is the most common radionuclide contaminant in subsurface systems associated with the U.S. Department of Energy (DOE) sites where nuclear materials were processed and stored. We have used a suite of atomistic simulation techniques to provide an atomic-level characterization of U properties in model systems relevant to DOE sites.

U preferentially associates with intra-grain domains in U-contaminated sediments collected from the DOE Hanford site and diffusion is expected to control the future mobility of U in these sediments. Therefore, we present molecular dynamics simulations of the diffusion and adsorption of uranyl carbonate species in intra-grain micropores, using feldspar-water fractures as a model system. Uranyl carbonate species dominate U(VI) aqueous speciation in Hanford groundwater conditions. The simulations show the effects of confinement and of the presence of the mineral surface on the diffusion of water and several uranyl carbonate species [1-3].

Uranium sorption by Fe-(hydr)oxides, which are common minerals in soil systems, has been conceptualized as a surface process; however, sorption is not necessarily reversible. The potential for incorporation into the mineral structure is supported by EXAFS studies; however, the evidence for incorporation rests on distances that do not match distances claimed for simple adsorption. Therefore, independent data are needed to confirm the structural incorporation hypothesis.

In this paper, we present atomistic modeling performed to evaluate the coordination of U incorporation in three Fe-(hydr)oxides [4]. The simulations provided information on U-O and U-Fe distances, coordination numbers, and lattice distortion for U in different sites and oxidation states. Comparison of the simulations with available experimental data provides further evidence to support the structural incorporation hypothesis.


Probing mineral-water interfaces with computer simulation

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The atomic-level structure of water at mineral surfaces is an important controlling factor in interfacial reactions. Therefore, differences in interfacial water structures could contribute to variations in surface reactivity between different surfaces of a single mineral. In this presentation, the water interfacial structure of three hematite surfaces, namely, the (012), (110), and (001) surfaces, will be contrasted [1]. An extensive comparison with X-ray scattering data provides further evidence that MD models can be used to reliably predict the structure of mineral-water interfaces. In addition, the MD trajectories were analyzed to gain insight into the surface structural controls on the interfacial water structure.

Mineral-water interactions also play an important role in carbonation reactions, which are one of the principal families of chemical interactions relevant to geological CO2 capture and storage (CCS). Although carbonation of minerals in contact with a CO2-containing aqueous phase has been extensively studied, carbonation reactions involving water-bearing supercritical CO2 fluids (WBSF) have received comparatively little attention. However, the limited number of studies published to date all highlighted the dependence of the extent and rate of reaction on the water content of the WBSF. Therefore, a detailed understanding of the structure of the WBSF-mineral interface as a function of water content is critical to elucidating the mechanisms of carbonation reactions in conditions relevant to CCS.

MD simulations of a model forsterite surface in contact with WBSF of varying water content were performed to determine the partition of water between the WBSF and the mineral surface and the nature of CO2 and H2O bonding at the interface. The simulations show that water readily displaces CO2 at the surface and that the formation of a water film at least three-monolayer thick can be exothermic even for water contents below saturation. The density, diffusion, and degree of hydration of CO2 as well as the extent of CO2/H2O mixing at the interface were all predicted to depend strongly on the water content of the WBSF.

Advancing studies of the origin and role of hydrocarbons in ore-forming systems

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We have advanced an in-line rock crushing, gas chromatographic (GC) technique that can detect and quantify hydrocarbons present within fluid inclusions to a lower limit of 1 ppm. This technique has been adapted from developments by Bray et al. [2] and Salvi and Williams-Jones [1] in order to comprehensively analyze a much wider range of hydrocarbons (C1-C9 olefins and paraffins). The system is comprised of four stainless steel rock crushers that crush rock fragments in a sealed and sterile environment, passing the released volatiles into the GC to be separated and analyzed.

Rock types associated with various ore-forming systems, as well as a number of others are being investigated. These include: mantle-derived xenoliths, hydrothermal veins from major ore deposit types including MVT, VMS and magmatic sulfide deposits, porphyry systems, IOCG deposits, and epithermal/geothermal deposits. With this work, we are: (1) constraining the importance of hydrocarbons in transporting ore metals via olefins, alcohols and/or carboxylic acids that may facilitate metal complexation and transportation; (2) determining hydrocarbon origin (e.g. mantle-derived, remobilized from associated hydrocarbon deposits, in situ formation by metal catalyzed Fischer-Tropsch reactions [3]).

We suspect that the presence of particular metals (i.e. group VIII elements [3]) may effectively catalyze the speciation/polymerization of light hydrocarbons into higher order compounds via the interaction between oxidized and/or reduced carbonic fluids within hydrothermal systems with various ore metal-bearing systems. Tentative results collected from analyzing hydrothermal quartz veins associated with base metal sulfide deposits in the Canadian Shield illustrate a high level of hydrocarbon speciation, including compounds such as butane, pentane, hexane and various saturated and unsaturated isomers thereof. Trace quantities of higher order compounds within the C6-C8 region were also found (possibly toluene, xylene, octane, etc.).


Metallogenic provinces: Products of asthenosphere-thermal boundary layer-lithosphere interactions

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Continental lithospheric mantle (CLM) was extensively modified by subduction-derived fluids especially at craton margins, and melts, from ~ 3 Ga as preserved in xenoliths of CLM. As well, melt-related metasomatism of CLM can be proxied by alkali basalts in ocean basins, by Dupal-type anomalies where a continental low-velocity zone is rafted into ocean basins as continents rift, and by continental alkali basalts all with high-LREE budgets.

Orogenic gold deposits, dominantly associated with accretionary-type orogens, are generated at terrane boundaries where an accretionary wedge, and LVZ, are subcreted between the over-riding and subducting plates. Dehydration at low-water-rock ratios, following cessation of subduction, generates low-salinity aqueous fluids enriched in Au, Ag, As, Sb, Hg and lithophile elements which advect along terrane boundaries where the deposits form. This element budget is a proxy for subduction-fluid induced metasomatism of the mantle wedge and sub-arc lithosphere during normal convergent margin magmatism.

During rifting of such metasomatised mantle in continental and oceanic settings, Au-rich fluids, and alkaline magmas, are generated as expressed in Au-porphyry deposits and epithermal systems. During plume impingement at craton margins ultramafic liquids interact with noritic melts generated from mesamatised CLM raising Si- and H2O-activities that trigger sulphide saturation for Ni-Cu-PGE deposits. At intracontinental rifts where plumes are focussed, the bimodal A-type granite and gabbro-anorthosite association is best expressed in the Proterozoic as controlled by the depth of the CLM. Fe-oxide, Cu, Au, REE deposits form by plume and decompressional melting and dehydration of metasomatised CLM with REE-contributed from entrained LVZ.
Glacial to Interglacial changes in the carbonate ion signature of deep and intermediate water masses in the Southern Ocean

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The Southern Ocean (SO) currently acts as a sink for CO₂, which is transported to intermediate [1] and deep waters [2] and consequently alters the inorganic carbon chemistry there. With regard to the rise in atmospheric pCO₂ since the Last Glacial Maximum (LGM), we aim to reconstruct fluctuations in [CO₃²⁻] in the Circumpolar Deep Water (CPDW) and the Antarctic Intermediate Water (AAIW) in the Australian and Pacific Sector of the SO. For this purpose, B/Ca ratios in benthic foraminiferal shells (C. wuellerstorfi, C. mundulus and Uvigerina spp.) are obtained. Deep water samples from the South Tasman Rise show a clear decrease in average B/Ca ratios from the LGM (43 µmol/mol) towards the Holocene (29 µmol/mol), from which we reconstruct average LGM and Holocene carbonate ion contents of 130 µmol/kg and 81 µmol/kg, respectively. Holocene values are corroborated by data from nearby GLODAP sites and the observed drop in seawater-[CO₃²⁻] is consistent with an increase in atmospheric pCO₂ since the LGM. Reconstructed values from Challenger Plateau sediments (bathed by AAIW) follow the trend observed in deep water cores, showing a decrease in average [CO₃²⁻] from 93 µmol/kg (LGM) to 81 µmol/kg (Holocene). Results from the shallowest core (958 m water depth) however reveal rising [CO₃²⁻], which might reflect location- and depth-related differences in CO₂ uptake and release. To investigate this further, we are currently analysing sediments from the SE of New Zealand, which stem from AAIW and CPDW depths. Moreover, a continuous [CO₃²⁻]-record for the last 20 ka will hopefully enable us to further constrain the temporal relationship between changes in SO carbonate chemistry and the step-wise release of CO₂ into the atmosphere.


Plutonium transport: Identifying the biogeochemical mechanisms controlling its behavior

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A major challenge in predicting the mobility and transport of actinides is determining the dominant biogeochemical processes that control its behavior in the subsurface. Plutonium (Pu) is of particular concern do to its large worldwide production inventory, high toxicity to human health and long half-life. There is more than 2200 metric tons of Pu throughout the world (ISIS website). The long half-life of Pu (²³⁹Pu ~ 2.4 x 10⁴ years) together with existing inventories guarantees that significant quantities will remain in our environment for a very long time. Effectively managing, controlling, and disposing of these materials in order to stop inadvertent release and transport through the geosphere is a serious scientific challenge. Currently, scientists cannot reliable predict how or how much Pu will move once deposited in the subsurface preventing accurate assessment of risk to human health. The behavior of Pu is complex because the reaction chemistry of Pu (i.e. aqueous speciation, solubility, sorptivity, redox chemistry, and affinity for colloidal particles, both abiotic and microbially-mediated) is particularly complicated. Its migration is known to be oxidation-state dependent and facilitated by transport on particulate matter (i.e. colloidal particles). Yet very little is known about how and under what geochemical conditions colloids facilitate the transport of Pu.

Despite the gaps in our understanding, recent field and laboratory experiments are helping to shape our conceptual understanding. I will summarize our current understanding of the biogeochemical processes controlling Pu transport by discussing recent field and laboratory studies. Field studies include weapons facilities where contamination of large quantities of Pu have been deposited and migrated in the subsurface. These studies demonstrate that colloids can and do play an important role in the transport of low-solubility radionuclides; yet, colloids are not always responsible for transport. It is becoming clear that the depositional history of the contamination, as well as the site-specific hydrogeology is critical to assessing the dominant biogeochemical processes controlling the migration of Pu. In addition, the dominant biogeochemical processes controlling migration of Pu can change along the flow path from the source to the far-field environment.
Magmatic evolution of the Eastern Anatolian High Plateau, E. Turkey

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The Eastern Anatolia High Plateau is an actively-deforming continental collision zone with a long-lasting volcanism from the end of Middle Miocene to historical times. It hosts some of the largest volcanic centers and plateaus of the circum Mediterranean region (e.g. Mt. Ararat, Nemrut, Tendurek and Suphan). Eastern Anatolia is a unique place in the world where the continental crust, most of which is represented by an accretionary complex, directly overlies the asthenospheric mantle [1]. So, the region is devoid of a lithospheric mantle. This unusual setting has been proposed to be linked to a major slab-steepening & breakoff event [1, 2].

To better understand the magma genesis and the geodynamic setting, we have been conducting a series of projects in E Anatolia since 2007, carefully studying the stratigraphy of the volcanoes and conducting radiometric datings and geochemical analyses. Results from our new and rather comprehensive database have revealed that the volcanism initiated around the N of Lake Van in the south at ~15 Ma with the eruption of calc-alkaline lavas containing a distinct subduction signature. The geochemical character of the volcanism changed from calc-alkaline to alkaline both in time (from Mid. Miocene to Quaternary) and space (from N to S), while the subduction signature temporally diminished. Our melting models suggest a region-wide temporal change from garnet- to spinel-dominated mantle mineralogy and an increase in the degree of melting. Our AFC and EC-AFC models indicate a significant crustal involvement increasing to the south. These findings may imply that the steepening of the slab has been a much faster event than we previously anticipated and the magma generation might have been influenced by the reformation of a new lithospheric mantle.


230Th–234U–238U disequilibria along the river catchments from the Iberian Belt (Spain) affected by acid mine drainage (AMD)


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The Tinto and Odiel Rivers can be used as a natural laboratory to investigate how changes in the aqueous environment affect the mobility of U-series nuclides. These rivers have very low pH’s of < 3 for most of their courses, as a result of acid mine drainage (AMD) processes. These AMD conditions generate preferential leaching of 234U compared to 238U from minerals in the background geological setting. Dissolved 238U activities vary from 10 to 850 mBq/L, with the highest 238U activities as well as the highest 238U/238U ratios (approaching 3.0) being present under the most acidic conditions. The acidic environment also promotes the dissolution of 235Th, whose activities are up to several orders of magnitude higher than are commonplace in most natural waters. The mobilities of U and Th decrease as pH increases, resulting in precipitation of uranium-bearing minerals in the estuary. The high concentrations of sulfate appear to have an important role in complexation of dissolved Th. These results direct relevance to predicting the mobility behavior of other particle-reactive actinides under acidic conditions in the surface environment.
Liesegang banding and biochemically mediated geochemical self-organization

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The Kanab Wonderstone is sandstone from the Shinarump member of the Chinle Formation that is variably cemented and stained with iron oxide. These sandstones contain approximately 5% Fe occurring as one to 5 mm thick, undulatory bands of iron oxide cement (IOC) that crosscut and obscure sedimentary structures. Between each pair of IOC bands are alternating bands of rock that are tinted with iron oxide stain (IOS) and unstained rock. The bands of IOS also crosscut and obscure sedimentary structures. The interior-most portion of the sandstone bed may contain a bleached sandstone core enclosed by a band of IOC. The IOC and IOS are related spatially to vertical joints that cut the sandstone at regular intervals. The IOC in the Shinarump comprises a mixture of acicular grains (goethite) and hexagonal plates with dendritic manganese oxide locally projecting from the cemented sandstone into more bleached rock. Although these features are unusual, they are not unique to the Shinarump member: similar features have been reported from other fluvial rocks worldwide. These features have been typically referred to as Liesegang bands, a type of geochemical self-organization.

The spacing of IOS is consistent with a Jablczynski coefficient [1] of 1.04 and the width of the IOS is a function of distance from the initial reaction front; characteristics that are typical of Liesegang bands [2]. Bands of IOC, on the other hand, exhibit more variable spacing and a relationship between IOC band thickness and distance between IOC. The Shinarump Wonderstone and similar rocks combine features of true Liesegang and biogenically mediated geochemical self-organization. Iron-oxidizing bacteria colonized the interface between siderite-cemented sand and porous sandstone, oxidizing iron and generating acid that caused dissolution of siderite. Aqueous ferrous iron diffused back to the biofilm where it was oxidized. Bands of IOS retain the morphology of reaction front fingers.


Origin and evolution of post-collisional volcanism: An example from Neoproterozoic Dokhan Volcanics at Gabal Nugara Area, Northeastern Desert, Egypt

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Nugara volcanics are one of the northernmost outcrops of the Arabian-Nubian Shield (ANS). Two distinct volcanic successions are found in the Nugara basin: (1) old volcanic sequence composed of voluminous medium- to high-K calc-alkaline lavas, and minor alkali basalt; and (2) young volcanic sequence composed of subordinate tholeiitic mafic lavas. Their eruptions were punctuated by occasional volcaniclastic deposits that generated fall, flow or reworked suites compositionally identical to the lava flows. These volcanics are a part of a post-subduction and extensional-related magmatic event in Northeastern Desert of Egypt.

Volcanic rocks of the Nugara basin are characterized by strong enrichment in LILE relative to HESF, high LILE/HFSE ratios and depletions of Nb on MORB-normalized multi-element diagrams. Geochemical features of the volcanic rocks suggest that they experienced fractional crystallization, along with mixing processes. Crustal contributions to the magma sources may also have occurred during magmatic evolution. These processes have resulted in scattered major and trace element variations with respect to increasing silica contents. The model proposed for their origin involves contrasting ascent paths and differentiation histories through crustal columns with different thermal and density gradients.

Geochemical features of the most mafic samples suggest that the volcanic rocks in the region were derived from a mainly lithospheric mantle source that had been heterogeneously metasomatized by previous subduction events during convergence between the East and West Gondwanaland. The volcanic activity in the region is best explained by delamination of lithospheric mantle slices that were heterogeneously enriched by previous subduction-related processes.

Hydrogeochemistry and origin of cold high pCO₂ waters of Gonjinskoe spa (Priamurye, Russia)

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Gonjinskoe is the most explored and popular spa with high pCO₂ groundwaters in the Priamurye. This spa is very actively used for treatments of gastrointestinal and heart diseases. In the last decade chemical composition of the spa was changed due to intensive exploitation so the main purpose of our study was to investigate the origin and evolution of the spa. Gonjinskoe spa is located in the Magdagachi area in the Valley of Bezimianniy River (Amur River basin) within the limits of the Mongolo-Okhotskaya geosynclinal area. Geologically, two rock formations were found of the study area. The oldest of these is Archeozoic metamorphic rocks of the Gonzhinsky horst. This formation essentially is composed of gneisses and marbles and often contains dykes of Early Cretaceous diorite and rhyolite. The tectonic structure of the spa is very complicated as two large regional faults northeast and sub-latitude directions are crossing here.

Groundwater mainly occurs in fractured Upper Cretaceous intrusive rocks of the area. Total area of the spa is 0.9 Km² and three boreholes are actively utilized now. Water samples were collected over a ten-year period; additionally some published data were re-interpreted.

Two types of groundwater were distinguished here: fresh and high pCO₂ ones. Both types of water are very cold, the temperature is 0.5-1.0 °C. Fresh water has very low TDS (up to 0.1 g/l) and belongs to Ca-Mg-Na-HCO₃ type. High pCO₂ groundwaters have TDS up to 3.5 g/l, CO₂dis. – 3.5 g/l and belongs to Ca-Mg-HCO₃ type. pH of waters very from 5.5 to 7.6.

Our bedrock and groundwater data indicates that both types of groundwater originate from meteoric water, and interactions between the water and these bedrocks have played a dominant role in the development of the chemical composition of the waters. Isotopic data indicates that CO₂ gas in the groundwater is mantle derived and its presence is critical for the development of the high pCO₂ groundwater. This type of groundwater evolves during gas-water-rock interactions only.

Flour content in the groundwater samples of Chahar-Farsakh area, South Khorasan, Iran

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The study area is located about 24 km NW Nehbandan, South Khorasan province, Iran. Chahr-farsakh area was occurred at Iran's East Flysh belt junction with Lut block. This junction is a thin zone of crushed disruption, fault corrosion, extreme drift and metamorphism. Igneous, metamorphic and sedimentary rocks as granodiorite, quartz diorite, andesite, sandstone, shale, conglomerate, gneiss and schist with many other type of altered and crashed rocks from Jurassic to Neogen are the most rock formation in the area. In this study, the concentration of flour in 20 samples of groundwater sources as qanat and spring were determined. The results of analyses show that flour content were determined to range between 0.02-0.84 mg/l, lower than WHO 2008 limits. Temperature of waters distinguished between 19.4-30.6 °C. The water PH were detected from 6.68 to 9.37. Flour show positive correlation with Na, Mg, Ca and HCO₃ in the water samples. Sandstone and shale seems to be the main aquifers in the study area. Mineralogical study by XRD shows that quartz is the main mineral in the aquifer and Illite, muscovite, shamosite, albite and calcite are subordinate minerals. Probably illite and muscovite are the main source of flour in the groundwater.
Boron contamination in the groundwater of Chahar-Farsakh area, South Khorasan, Iran

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Groundwaters from 6 qanat and spring stations within the Chahar-Farsakh area, north-west of Nehbandan, South Khorasan province, Iran were sampled for metal contamination analysis. The data were used to calculate metal index (MI), all of the groundwater samples show metal index higher than 1. Among all analysis results, boron show high concentration in the groundwater samples. Concentrations of B in water samples from Chahar-Farsakh area were determined to range between 1.043-4.811 ppm, exceeding WHO (2009) limits (0.5 mg/L) for drinking waters. Naturally occurring boron is present in groundwater primarily as a result of leaching from rocks and soils containing borates and borosilicate. Geological surveying in the study area revealed some outcrops of pegmatite aplitic veins with tourmaline mineralization. Probably existence of tourmaline is the major natural source of boron in the water samples of Chahar-Farsakh area.

Petrography and mineralogy of Western Samen Metapelites

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The study area is located in southern of Hamadan, Sanandaj-Sirjan zone. Metamorphic rocks involve philit and Schist with green schist facies, advanced to amphibolite facies. These rocks composed of various metamorphic minerals. EPMA analysis is applied on some mineral to recognition of chemical composition of rock forming minerals. Mineral chemistry shows Muscovites that formed in rim of andalusite, have higher grade than those are in matrix and resulted of progressive metamorphism of andalusite to Muscovite, Staurolite and Fibrolite. Also Biotites are ferric and garnet is almandine and belongs to Piralespite groupe. Zoning pattern in garnet imply two progressive metamorphism and a retrogressive metamorphism that preserved in some garnets. Analytical data only show the composition of Staurolite.
Natural cementitious analogues of Jordan
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The pyrometamorphic rocks in Jordan (Daba-Siwaqa, Suweileh and Maqarin) are unique and represent natural analogues of Portland cement for sealing of nuclear waste. The natural occurrences are of great aerial exposure and offer good example to study the interaction of cementitious hyperalkaline leachates on repository host rock. Similarity to cement processes and products is much more obvious than in any of the occurrences reported before. The similarity extends beyond strong mineralogical equivalence. The source of energy for this extremely energy intensive process was the same as cement kilns (fossil fuel from oil shale).

Maqarin area represents an early stage in the evolution of cementitious repository.

Suweileh and Daba-Siwaqa areas represent a later stage. Results on natural analogues in Jordan indicate that secondary minerals as smectites, sulphates, and hydrated aluminium silicates act as a sink for hazardous elements. Highly alkaline (pH = 12.7) ground water dissolves from the combusted bituminous marl the radionuclides and heavy metals (Cr, Zn, V) and reprecipitate it farther down when reducing conditions are encountered [1].


Photochemical production of dissolved organic and inorganic nutrients from resuspended sediments
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A series of photolysis experiments were conducted in the presence and absence of tidal creek and continental shelf sediments to address the role of resuspension on nutrient fluxes in estuarine and coastal waters. There was a significant increase in TDN, phosphate and DOC when sediments were resuspended in overlying water and exposed to six hours of simulated sunlight. The majority of dissolved N was released as DON (87%) with relatively lesser amounts of ammonium (13%) and little or no nitrate. Results from autoclaved sediments suggest the mechanism of photolytic release was predominately abiotic. Results demonstrate that photoproduction from resuspended sediments is an episodically significant and previously unrecognized source of dissolved nutrients to coastal ecosystems receiving sediment plumes. This process may be especially important for continental margins where resuspension events occur as well as in regions experiencing high riverine sediment fluxes resulting from erosion associated with deforestation and desertification. The presentation also considers how photolytic fluxes of organics and nutrients may respond in the future during periods of salinity alteration as sea level rises.
Biogenic volatile emissions and their contribution to organic aerosol mass

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Land vegetation contributes 90% of the global volatile organic compound (VOC) emissions [1]. Atmospheric oxidation of these VOCs contributes to new particle formation and atmospheric organic aerosol mass [2]. The formation of aerosols from biogenic VOC emissions constitutes a possible feedback element in biosphere-atmosphere-climate interactions due to the overall cooling effect of aerosols [3]. This is based on increasing VOC emission strengths with increasing temperature and emission patterns being invariant to temperature changes. Recently evidence emerges that temperature induced changes in VOC emission patterns may alter the picture. It has been shown that increased isoprene emissions may suppress atmospheric new particle formation [4] thus dampening the cooling effect of aerosols formed from biogenic VOCs.

In addition the use of direct emissions of VOCs from plants in experiments studying secondary organic aerosol (SOA) formation shows that, beyond the so far considered main compound classes isoprene and its derivatives monoterpene and sesquiterpenes, other VOC classes significantly impact SOA formation. Many of these VOCs are emitted under plant stress conditions.

An overview of the state of the art knowledge of SOA formation from biogenic VOCs with respect to different VOC classes will be given. In particular we will focus on the importance of non-classical VOC classes emitted under stress conditions.


Factors affecting the stability of slags and metal release: The case study of historical Cu slags from Lower Silesia (SW Poland)

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Historical slags originating from base metal smelting often contain considerable amounts of heavy metals and, when deposited, they may undergo potentially harmful interactions with surrounding soils, sediments and waters.

In this study we present mineralogical and chemical characteristics of historical slags from Rudawy Janowickie Mountains (Lower Silesia, SW Poland). We show that the studied slags are characterized by different cooling rates of the slag melt and we describe how these different rates affect slag properties (phase composition, metal distribution etc.). Furthermore, on the basis of leaching experiments, simulating various environmental conditions, we attempt to identify major factors controlling heavy metal release from slags.

Two types of slags produced during historical smelting of Cu ores occur in the studied area. The prevailing massive slag consists of silicate glass, olivine and hercynite. The second type is porous and comprises two types of silicate glass, olivine, ferrosilite, cristobalite and quartz. Both types contain important amounts of metals (up to 1.34 % of Cu).

The morphology of olivine crystals, phase assemblages, phase chemistry and distribution of trace elements in slag phases vary from sample to sample, which is consistent with different cooling rates. Careful investigation of cooling conditions is useful to predict susceptibility of slags to weathering. Leaching tests, performed on each type of slag show that the heavy metal release is more important for porous slags than for those having massive texture. Furthermore, larger proportions of heavy metals are released from slags formed under disequilibrium conditions than from those which cristallized under close to equilibrium conditions.

Mineralogical and geochemical analyses coupled with leaching experiments indicate that the most important factors controlling metal release from slags are: (1) textural characteristics and permeability of the material, (2) slag mineralogy and cooling rates, (3) environmental conditions (e.g. pH, organic matter content).

The work was financed by Polish Ministry of Science and Higher Education grant no. NN307051237.
Fluid microinclusions in octahedral diamonds

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Microinclusions carrying high-density fluids (HDFs) with silicic, carbonatitic and saline compositions are common in fibrous diamonds and represent the medium in which their host diamond grew. Such inclusions have not been documented previously in monocrystalline octahedral diamonds or in the octahedral cores of coated diamonds, allowing a debate on whether such fluids are responsible for the formation of octahedral diamonds as well. The other notable difference is that all nitrogen in microinclusion-bearing zones resides in A-centers, whereas most octahedral diamonds carry both A and B centers. We report the first finding of HDF microinclusion in an octahedral diamond from Finsch, South Africa and in the core of a coted diamond from Kankan, Guinea.

The microinclusions in the Finsch diamond are restricted to two thin layers (~10 µm), parallel to the (111) face, ~20 and 200 µm from the rim. Cathodoluminescence (CL) reveals concentric zoning and octahedral growth throughout the diamond. The inclusion-rich layers are easily recognized by their weak fluorescence. The diamonds carry ~800-1200 ppm nitrogen. Absorbance of B centers is observed in the inner part (A/B=5) and between the inclusion rich layers and the rim (A/B=16). Forty-five inclusions of carbonatitic HDF were analyzed along the inner layer. Their major and trace element compositions and FTIR analyses are highly similar to the ones observed in HDFs from fibrous diamonds.

In the octahedral core of the Kankan diamond we found six microinclusions with saline composition. Unlike the case of the Finsch diamond, these inclusions are sporadically scattered, up to ~100 µm away from a sulfide mineral inclusion and were hard to find.

Supporting evidence for the involvement of HDF, similar to the ones capsulate in fibrous diamonds, in the formation of monocrystalline diamonds comes from LA-ICP-MS analyses of trace element patterns in monocrystalline diamonds (McNeill et al. 2009) and the sinusoidal REE patterns of garnet inclusions in diamonds (Stachel and Harris, 2008; Weiss et al. 2009).

Based on the above observation we have good reasons to believe that microinclusions and HDFs may be found in other octahedral diamonds, extending the role of HDFs to the formation of most natural diamonds.

Seasonal and temporal variations of uranium isotope ratio in atmospheric deposits in Japan

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The uranium isotope ratios, especially $^{235}$U/$^{238}$U, do not change substantially in the natural environment. The $^{236}$U/$^{238}$U ratio in environmental samples differing from the natural ratio thus resulted from anthropogenic nuclear activities. The Japan Meteorological Agency (JMA) and the Meteorological Research Institute (MRI) have been monitoring the deposition amounts of anthropogenic radioisotopes, mainly $^{90}$Sr and $^{137}$Cs, using the atmospheric deposits collected with open surface samplers installed throughout the Japanese Islands since the 1950s. In our previous work, we had reported that the $^{236}$U/$^{238}$U ratios in the deposits collected at Fukuoka, Kyushu, the most southwesterly one of the four Japanese main islands, were slightly but obviously higher than the natural ratio since the 1960s until today [1]. This time, we have measured the uranium isotope ratios in the atmospheric deposits collected at Akita, which is located at the northeastern region of Japan and faces to the Sea of Japan, in the months of March between 1964 and 2000 and every month in 1977 and 1978. The results revealed that the $^{236}$U/$^{238}$U ratios in the atmospheric deposits had varied seasonally and temporally. The fluctuation pattern of the $^{236}$U/$^{238}$U ratio in the Akita deposits through the 24 months in 1977 and 1978 is in good accordance with that of the deposition amounts of plutonium at Tokyo [2]. Contrary to this, the deposition amounts of $^{90}$Sr and $^{137}$Cs are not always connected with the uranium isotope ratio in the deposits. Our results suggest that a certain amount of depleted uranium (DU) had been transported to Japan in the 1970s with plutonium ejected into the atmosphere by the thermo nuclear tests then conducted in the test sites in the Central Asia. DU and plutonium had probably been transported by the mechanism different from that of radioactive strontium and cesium, although they all had come from the same source, neuclear test explosions.

Speciation of iron in natural and synthesized Bacteriogenic Iron Oxides (BIOS) using XAFS and μ-XRF-XAFS

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Speciation of Fe in natural and synthesized bacteriogenic iron oxides (BIOS) was studied using XAFS, μ-XRF-XAFS, SEM and EPMA. Natural BIOS were collected at 2 sampling sites: seafloor at Mariana trough and from groundwater stream discharged at Sambe Hot Spring in Shimane Prefecture. BIOS was synthesized using a diffusion cell which consists of two cells that are separated by a membrane. Anoxic and oxic conditions were created in each cell to simulate the appropriate condition to BIOS precipitation in natural environment. Chemoautotrophic iron-oxidizing bacterium (Mariprofundus ferrooxydans [1]) or heterotrophic iron-oxidizing bacterium (Leptothrix discophora [2]) were cultured in the oxic cell.

SEM and EPMA analysis suggested similar precipitation morphology to all samples where iron oxides precipitated around bacterial-induced organic materials. Although each natural BIOS were precipitated in different environment, the XAFS spectra exhibited similar structures. Synthesized BIOS also showed spectra similar to natural samples regardless of the species of iron oxidizing bacteria and the medium employed in culture. In addition, μ-XAFS spectra collected at several Fe-precipitated area within few micro scale in the stalk were approximately identical, which is consistent with our bulk XAFS results of natural and synthesized BIOS. These results suggest that minerals presented in BIOS were homogeniously distributed in micrometer scale. The linear combination fitting suggested that ferrhydrite is one of the Fe species in BIOS. It is also implied that Fe-carboxylate complex or Fe (III)-phosphate is a second Fe species of BIOS. These results will provide better insights into understanding the role of BIOS in the migration of trace elements in natural waters.


Origin of ultramafic rocks from Hero Fracture Zone, Antarctic

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Serpentinites are rocks composed predominantly of the serpentine minerals, lizardite, chrysotile, or antigorite that form through hydrothermal alteration of peridotite. Substantial exposures of serpentinized peridotites are commonly found in fracture zones and in slow spreading mid-ocean ridge settings. Serpentinites from the Hero Fracture Zone, Drake Passage, Antarctica, contain serpentine, amphibole, talc, chlorite, and magnetite as well as relict olivine, pyroxene, and spinel from a spinel peridotite precursor. Two episodes of serpentinization are recognized. The initial serpentinization event resulted in material that contains relatively abundant relict minerals and small amount of lizardite and antigorite. This event resulted from seawater infiltration at about 178 - 283 °C seawater and a water/rock ratio less than 5. The second serpentinization event resulted in a material highly enriched in serpentine. This second event was caused by seawater infiltration at 170 - 298 °C and a water/rock ratio in excess of 5. The buoyant serpentinite ridge model is invoked to explain the ascent of serpentinite from the upper mantle to the surface. Increasing fracturing and seawater infiltration during the process resulted in increasing degrees of serpentinization and decreasing rock density. Buoyant uplift of serpentinite resulted from the contrast in density between serpentinite and surrounding mafic rocks. Some serpentinite rock fragments were detached from the serpentinite during ascent and embedded in oceanic sediment after exposure to the surface.
CO₂, CH₄, N₂O flux measurements from a constructed wetland

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Implication
It is recently reported that microbial activity in freshwater wetland soils transforms considerable amounts of CO₂ into CH₄, which is then released into the atmosphere [1]. Consequently, this is likely to enhance greenhouse effect as CH₄ has a global warming potential greater than CO₂. The current study was focused on quantifying the source strengths of these greenhouse gases (GHG) from a wetland water surface and elucidating relationship between GHG emissions and physicochemical parameters.

Sampling and Experimental Methods
A closed chamber system was utilized to measure GHG emissions from water surface in a constructed wetland at Kunsan, Korea for six-month period (August-December, 2010 and March 2011). The measurements were made on 20 days during a day time (1400-1600LST) for experimental period only when weather was clear, and 50 ml of three consecutive gas samples for one GHG flux calculation were taken at each 10 min interval from a half spherical plastic chamber floating on the wetland water surface with plastic syringes. GHG fluxes were calculated based on the rate of change of GHG concentration [2]. Chemical characteristics in water (NO₃--N, NH₃+-N and pH) and water temperature also were monitored on measurement days. Concentrations of CO₂, CH₄ and N₂O were analyzed by using a Gas Chromatography (equipped with ECD/FID) at laboratory.

Results and Discussion
In order to examine the role of temperature on the gas flux, the changes of GHGs’ emissions were investigated in terms of water temperature measured during sampling period (warm season: 18-31 °C, cool season: 8-12 °C). Results from current wetland experiment shows that water surface of the wetland absorbs CO₂ (sink) and emits CH₄ and N₂O (source) in average over the experimental period. Those levels were greater in warm season than in cool season. Further results in correlations between physicochemical controlling parameters and those GHG emissions will be discussed in the conference.

This work is supported by NRF Korea Grant (2009-0072936).


The elemental and stable isotope geochemistry of Korean bottled waters: Characterization and identifying their origins

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We investigated 54 Korean bottled waters to characterize their water types and to examine a good tool for identifying their origins using the elemental and isotopic geochemistry. The elemental and isotopic compositions of the bottled waters varied substantially in different types of bottled waters. Major ion chemistry and oxygen and hydrogen isotopes clearly discriminate marine waters from the other types of water. Fractionation of oxygen and hydrogen isotopes likely explains the altitude and latitude effects. Variations in dissolved inorganic carbon isotope values reflect artificial CO₂ addition in sparkling waters, and reveal fractionation during the desalination process of marine waters. Strontium isotope ratios (⁸⁷Sr/⁸⁶Sr) of bottled waters are clearly associated with those of basement rocks in which bottled waters were collected. The results suggest that combined elemental and stable isotope variations in bottled waters are useful for characterizing the bottled waters and identifying the origins. Furthermore, combined elemental and isotope geochemistry could be a powerful tool in the related research fields and forensic sciences.

Figure 1: Ternary diagram showing chemical characteristics of bottled water.
Stability of schwertmannite sorbed by oxyanions

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Schwertmannite, commonly found iron-oxyhydroxy sulfate in acid mine drainage has high sorption capacity and can play an important role in removing heavy metals in acid mine drainage. Heavy metals existing as oxyanions are known to have high affinity to schwertmannite compared with other heavy metals due to substitution for sulfate in the schwertmannite structure. However, schwertmannite is thermodynamically unstable and eventually transformed to goethite. The oxyanions such as AsO$_4^{2-}$, however, has been known to decrease the transformation rate. We made oxyanion-sorbed schwertmannite samples and studied their rates of transformation to goethite based on XRD patterns and pH values.

Schwertmannite was synthesized and oxyanion-sorbed schwertmannite was prepared by AsO$_4^{2-}$, SeO$_3^{2-}$, SeO$_4^{2-}$, MoO$_4^{2-}$, and CrO$_4^{2-}$. Because of the different sorption isotherms, the amount of sorbed oxyanions were fixed at 0.5 mmol/g for the samples. 0.1g of each samples were mixed with 40 ml distilled water and pH was adjusted at pH 9 at 30 $^\circ$C to increase the transformation rate. The pH was measured every week pH values were adjusted to pH 9 again. The experiment was conducted for 3 months and during that period, 3 samples of each schwertmannite were analysed by XRD and compared.

Our results show that all the samples sorbed by oxyanions have slower transformation rate than pure schwertmannite, indicated by higher pH values. However, the transformation rates among oxyanions are different. Based on the pH value changes, the transformation rates to goethite are in the order of pure schwertmannite > SeO$_4^{2-}$ > SeO$_3^{2-}$ > CrO$_4^{2-}$ > MoO$_4^{2-}$ > AsO$_4^{2-}$. XRD pattern of each sample shows that pure schwertmannite transformed to goethite after 1 month. After 3 months, the schwertmannite sorbed by SeO$_4^{2-}$ almost transformed to goethite while other samples still have schwertmannite peaks. Therefore, the XRD patterns and pH values are quite closely matched. Our results show that sorption of oxyanions on schwertmannite decreases the transformation rate to goethite, and the rates of each samples are different.

Relations of arsenic concentrations among groundwater, soil, and bedrock in Geumsan, Korea: Implication for As mobilization according to changes in As-hosting minerals and land use

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Arsenic concentrations and As-bearing minerals in bedrock, and soil, and their relations with groundwater concentrations were investigated in a small agricultural area of Korea to understand the changes in arsenic mobility by pedogenetic processes and changes in geochemical conditions. The arsenic concentration in bedrock shows a wide variation (<1 to 3990 mg/kg) and is well correlated with that in contacting groundwaters. Soils, the weathering product of bedrock, show much mitigated and dispersed, but still very high As concentrations (8.8 to 387 mg/kg). Furthermore, As concentrations in the shallow groundwaters were very low (<20 µg/L) and independent on the soil concentrations due to the differences in As hosts and geochemical conditions. Arsenopyrite is the major As-bearing mineral in bedrock and its oxidation controls the As levels in deep groundwater. In contrast, the As mostly resides in soil as Fe-(hydr)oxide bound forms. Due to low pH and oxidizing redox condition, the release of As from Fe (hydr)oxides are largely suppressed and the shallow groundwater show low As concentrations. However, it is suggested that the disturbance of geochemical conditions in soils by land use changes mobilize As and would cause serious As contamination in shallow groundwaters.
**Hypoxia events in Cheonsu Bay, West coast of Korea, triggered by discharge of eutrophicated water from artificial lakes**

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Frequent outbreaks of hypoxic water masses have been reported in Cheonsu Bay, west coast of Korea, due to the influx of eutrophicated waters heavily loaded with oxygen demanding material from artificial lakes formed by large-scale land reclamation and subsequent industrial development and rapid urbanization since early 1980s. The hypoxia events would give deteriorative impact on fisheries and aquaculture industry around the bay.

In summer 2010, we measured the concentration of dissolved oxygen (DO) and nutrients in bottom waters collected from 14 stations. We also measured the nutrient fluxes across the sediment-water interface in 3 stations by deploying a fully automated benthic lander, which collects time-series water samples inside a benthic chamber, on the seafloor for a couple of days.

We confirmed the on-going hypoxia in the northern parts of the bay into where the lakes discharged. DO content of the bottom water was below 2 mg/L, compared to that of 5 mg/L at the mouth of the bay. Organic carbon oxidation rate was estimated to be 55 mmol C m⁻² d⁻¹ and the oxygen consumption rates to be 50.4 mmol O₂ m⁻² d⁻¹. These rates were about twice as fast as those at the bay mouth. Benthic fluxes of nutrients at the northern part of the bay were 4 to 6 times higher than those at the bay mouth.

Our results imply that it is necessary to keep keen eyes on hypoxia events since they would give severe damages to fisheries and aquaculture industry.

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**Oxygen isotope fractionation between calcium carbonate and water: Influence of ionic strength**

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The conventional carbonate-water thermometer is one of the most successful paleotemperature proxies in the Earth sciences and it was developed on the theoretical basis of oxygen isotope fractionation between CaCO₃ and H₂O. As a result, numerous scientists have extensively studied the oxygen isotope systematics in the CaCO₃-H₂O system over the past several decades in order to establish a more reliable carbonate-water paleothermometer. Whereas the majority of natural calcium carbonate samples, such as corals and foraminifera, that are frequently used to reconstruct Earth’s past climate changes on the basis of the conventional carbonate-water thermometer, are of oceanic origin, most of the experimental studies, that provide a baseline for the calibration of many of the species-specific carbonate-water paleotemperature proxies [1, 2], used calcium carbonates precipitated from parent solutions of low ionic strength (e.g. freshwater) rather than those precipitated from parent solutions of seawater salinity or ionic strength (e.g. ocean water).

In order to investigate the effect of a parent solution’s ionic strength on the oxygen isotope fractionation between CaCO₃ and H₂O, calcium carbonates were synthesized in the laboratory from Na- Ca-(Mg)-Cl-HCO₃ solutions of seawater ionic strength (I = ~ 0.7). Subsequently, the oxygen isotope composition of the calcium carbonate precipitates and that of the parent solutions were determined. In particular, the passive CO₂ degassing and the constant addition methods, which are described in Kim et al. [3], were employed in this study. Our preliminary experimental results suggest that the oxygen isotope fractionation factors determined from calcium carbonates that were formed from high ionic strength solutions may not be always the same as those determined from low ionic strength solutions.

**Extinction-to-backscatter ratio of Asian dust observed with a combined Raman elastic-backscatter lidar in Seoul, Korea**

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The extinction-to-backscatter ratio (so called, lidar ratio), which is a key parameter in the issue of backscatter-lidar inversions, of Asian dust was observed with a combined Raman elastic-backscatter lidar in Seoul, Korea. The lidar ratio at 532 nm is calculated by the comparison of lidar-derived aerosol optical thickness (AOT) with sunphotometer-derived AOT for 4-year measurements (2006-2010). Here, the value of AOT 532 nm is calculated by the Ångström relationship using measurements at five wavelengths (400, 500, 675, 870, and 1020 nm). The annual mean lidar ratio (with standard deviation) is found to be 61.7±16.5 sr, and weak seasonal variations are noted with a maximum in summer (68.1±16.8 sr) and a minimum in winter (57.2±17.9 sr). The lidar ratios for clean, dust, and polluted conditions are estimated to be 45.0±9.5 sr, 51.7±13.7 sr, and 62.2±13.2 sr, respectively. While the lidar ratio for the polluted condition is appears to be consistent with previous studies (50-70 sr), clean and dust conditions tend to have larger values, compared to previous estimates (clean: 30-40 sr, dust: 40-50 sr). This discrepancy is thought to be mainly due to the anthropogenic aerosols existing in the atmospheric layer throughout the year around Seoul, which may cause increased S_a even for clean and dust conditions. For instance, the lower values of lidar ratio at 532 nm was directly estimated from Raman (inelastic) signals. The values of lidar ratio averaged for Asian dust layer was ranged from 25 and 40 sr on two Asian dust days (October 20, 2009 and March 15, 2010), with 10 ~ 20% of particle depolarization ratio.

**Dependence of adiabaticity of stratiform clouds upon stability, and its relationship to aerosol-cloud interactions**

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The buffering mechanisms in the modifications of cloud microphysics and cloud albedo by cloud-active aerosol are only vaguely understood and are thought to include a myriad of processes that vary regionally and confound the application of simple physical models of cloud-aerosol sensitivity [1]. This study presents the relationship of aerosol-cloud interaction to cloud environment condition (adiabaticity and stability), using data from the Atmospheric Radiation Measurement (ARM) Southern Great Plain (SGP) site and the Pt. Reyes (PYE) deployment of the ARM Mobile Facility (AMF). Adiabaticity is defined as the ratio of the observed liquid water path (LWP) to corresponding adiabatic value in this study. The stability indicates the differences of potential temperature between 500 m above the mixed layer tops and the mixed layer tops. Strong inversions above the PYE cloud are shown to buffer marine stratuscumulus from the effects of mixing with drier, warmer inversion air. This buffering reduces the variability of the cloud LWP and enables the clouds to remain nearly adiabatic. The critical comparison of cloud adiabaticity with static stability demonstrates the more adiabatic LWP in the condition of the stronger stability above the cloud. Weaker inversions above the SGP cloud promote variability in the LWP and sub-adiabatic LWPs. Aerosol-cloud interactions are probably more dominant in stratiform clouds that remain nearly adiabatic [2] and exhibit less variability in the LWP. This study implies static stability and adiabaticity are important controlling factors in the enhancement or attenuation of aerosol-cloud interactions.

This work was supported by the ‘National comprehensive measures against climate change’ by the ministry of environment, Korea (Grant no. 1600-1637-301-210-13).

Uranium minerals in black shale, South Korea

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Uranium (U) in black shale, South Korea has been the subject of interest because of its potential roles in energy and mining industries. Previous reports found that balck shale in Korea is highly metalliferous with lead, uranium, and vanadium, but also that uranium content increases with increasing total carbon content in the black shale. Yet, identification and understanding of minerals for uranium and other elements in the black shale is still not clearly addressed. In the present study, U-containing minerals in the black shale is characterized by combination of geochemical compostion analysis and electron probe microanalyzer (EPMA) analysis. Results show that uranium content is moderately proportional to the content of total organic carbon (TOC) in the black shale. XRF analysis shows that Al, Mg, Ba, and K are major elements with trace elements such as Zn, P, S, and Ti. Total uranium concentration is up to 0.13 wt. %, whereas total concentration of V and Ba are 0.17-1.6 wt. %, and 2.0-5.0 wt. %, respectively. Using EPMA, it is found that two different element series of U-P-Cu and U-V-Ba are found in U-containing minerals. Ratio of the series for U : V : Ba and U : P : Cu are 2 : 2 : 1 and 4 : 4 : 1, respectively. These results indicates that the U-containing minerals are francevillite ((Ba, Pb)(UO2)(V2O8)(H2O)) and torbernate (Cu(UO2)2(PO4)2(H2O)8) in the black shale. These findings are not consistent with previous reports showing that uraninite is a main mineral in U-containing minerals at a different area of the black shale, Korea. Upon our results, it is worthy to note that formation of uranium minerals are sensitively affected by geochemical environments and tectonic movements in the black shale, South Korea.

Mineralogical Magazine  www.minersoc.org

Uptake and retention of mercury by hydroxylapatite

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Mercury (Hg) is well known as a toxic element for humans and ecosystems. Partitioning of the mercury to minerals and organics has been known to influence the fate and transport of mercury species in natural ecosystems. Despite the importance of mercury interaction with minerals, sorption mechanisms and modes are are not still clearly understood. Systematic characterization of mercury uptake by hydroxylapatite (HAP, [Ca10(PO4)3(OH)]) is little addressed over a wide range of physicochemical conditions. Mercury sorption on HAP shows that the initial uptake of mercury by HAP sharply increases, levels off, and then followed by little changes as a function of concentration at pH 7.0 and 9.0, showing a typical pattern of Langmuir sorption. No obvious differences are found in the sorption pattern at the two pHs. Compared to that of the sorption at pH 7.0, however, the sorption of mercury on HAP decreases by a factor of 4 at pH 9.0. In addition, the mercury uptake by HAP decreases with increasing ionic strength of the solution. From I = 0.01 M to I = 0.1 M, total amount of the sorption decreases around by a factor of 2. During the duration of the kinetic experiments, the initial uptake and retention of mercury by HAP is rapid and ~85% of Hg is sorbed on the HAP within 30 mins, suggesting that adsorption plays an key role in the initial uptake of mercury at the HAP-water interface. Results reveals that different physicochemical conditions such as pH and I influence the mercury uptake by HAP sensitively.
Biogeochemical behaviour of Pu in a contaminated soil from Aldermaston, UK

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Understanding the biogeochemical behaviour of actinides in the environment is essential for the long-term stewardship of radionuclide-contaminated land. Plutonium is of particular concern due to its high radiotoxicity, long half-life and complex chemistry. Here, we investigate the biogeochemistry of Pu in a contaminated soil as microbial processes have the potential to mobilise Pu via the reduction of Pu (IV) to the potentially more mobile Pu (III). A series of microcosm experiments were designed to monitor changes in Pu solubility in an anaerobic environment stimulated via the addition of 10 mM glucose to Pu contaminated soils. A substantial shift in the 16S rRNA gene profile was observed between days 0 and 44 most notably with an increase in Clostridia, known glucose fermenters that have been reported to facilitate the reduction of Pu (IV) to Pu (III) [1]. A minor increase in Pu solubility was observed at day 44, decreasing to initial levels by day 118. The negligible change in Pu solubility, despite the onset of reducing conditions and formation of Fe (II), would suggest the Pu is highly refractory and unsusceptible to the influence of the surrounding geochemistry. To further examine the geochemistry of the Pu, a series of sequential extractions were performed. Around 75% of the Pu from the Aldermaston site was found to be associated with the highly refractory, residual fraction of the soils. This value greatly exceeds the fraction of residual Pu at other nuclear sites reported in the literature after similar extraction protocols (34% at Sellafield and 8% at Dounreay [2]) and further suggests the Aldermaston Pu is highly resistant to changing geochemical conditions. Further work is currently being undertaken to investigate the impact of citric acid producing fungi on Pu solubility as citric acid has the potential to mobilize Pu. This information is important for understanding both the long-term mobility of Pu in the environment and for developing remediation options for Pu-contaminated soils.

Interfacial reactions during olivine replacement
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Olivine-fluid interactions have a variety of applications in environmental remediation schemes, e.g., CO2 sequestration and sulphate-rich acidic solution neutralization. We have conducted experiments to examine olivine reactivity within these systems, including mineral carbonation (200 °C, carbonated saline solution) and sulphuric acid neutralization (90 °C). Furthermore, we have used in situ phase-shift interferometry (PSI) to gain new insights into surface specific olivine dissolution.

The role of the interfacial solution composition was most pronounced in experiments with sulphuric acid, which produced an amorphous silica pseudomorph after olivine at high acid concentrations. Incorporation of 18O into the silica layer in an isotopic tracer experiment indicates that the replacement reaction occurred via an interface-coupled dissolution-reprecipitation mechanism. The formation of a pseudomorph in 3.6 M and 2 M solutions suggests that at these conditions olivine dissolution was the rate-limiting step. However, in 1 M solutions the formation of the amorphous silica layer controlled the rate, uncoupling the spatial relationship between dissolution and reprecipitation so that no pseudomorph was produced.

Dissolution of different olivine surfaces in saline solutions were studied with PSI, and showed that the fastest dissolving surface supersaturated the interfacial solution to precipitate a new phase at acidic conditions. This phase is predicted to be similar to the amorphous silica-enriched phase observed to form in the carbonation experiments indicating that the interfacial solution composition plays a critical role under a wide range of conditions.

Sulfur isotope studies in organic matter via SIMS using a statistical approach with heterogeneous standards
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Solid bitumen, often found in rocks associated with a hydrocarbon phase, retains a paleo-signature reflecting the evolution of the hydrocarbon. For example, the 34S/32S ratio can provide information on the relative importance of thermal sulfate reduction over bacterial sulfate reduction during diagenesis. Such bitumen, distributed as small globules or grain coatings throughout the rock matrix, is a challenge to analyze. A technique with high-spatial resolution, Secondary Ion Mass Spectrometry (SIMS), is an excellent method, but there are challenges in applying this technique to such materials.

SIMS analysis of mineral phases is readily performed because standards allowing correction for instrument and matrix isotope fractionation have been developed. There are no comparable standards for sulfur isotopes in bitumen. Here we introduce the use of sulfur-bearing organic solids such as petroleum coke as such standards. They posses the required similarity in chemical bonding environment to that in bitumen. However to utilize these solids required that we develop a method to overcome their intrinsic chemical inhomogeneity. For example, there are finely divided sulfate phases distributed in the organic matrix. Utilizing SIMS imaging to avoid secondary phases and a statistical analysis technique to mitigate the influence of unresolved secondary phases, we found that consistent correction factors for both instrument and matrix fractionation can be obtained. We have generated a Calibrated Matrix Correction that allows the systematic analysis of δ34S values for bitumen, demonstrating those results by analyzing several bitumens from Brooks Range, Alaska and LaBarge, Wyoming.
Geocosmochronometer $^{146}$Sm: A revised half-life value

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Alpha-decaying nuclide $^{146}$Sm, now extinct, was extant in the Early Solar System (ESS) [1] and was proposed as a cosmochronometer measuring the time between $p$-process nucleosynthesis and ESS condensation. Positive isotopic anomalies in the $^{142}$Nd daughter have been measured in Earth rocks [2] and in Moon [3] and Martian meteorite [4] samples, relative to chondritic meteorites. This indicates that geochemical fractionation between Sm and Nd occurred while $^{146}$Sm was still live, possibly during mantle differentiation. These issues stress the importance of $^{146}$Sm half-life, now determined as $(1.03\pm0.05)\times10^{10}$ yr [5, 6]. We have performed a new determination of the $^{146}$Sm half-life by measuring both alpha-activity ratio and atom ratio of $^{146}$Sm to $^{144}$Sm at $(1.07\pm0.09)\times10^{11}$ yr [7]) in artificially activated $^{147}$Sm. The new value of $^{146}$Sm half-life, $(0.68\pm0.07)\times10^{8}$ yr, is significantly shorter than previously measured and will have interesting implications for the chronology of $p$-process and planetary differentiation. The experimental determination of $^{146}$Sm half-life will be described and discussed.

This work is supported in part by a Grant-in-Aid for Scientific Research Program of Japan Society for the Promotion of Science (20740161). This work is supported by the U.S. Department of Energy, Office of Nuclear Physics, under contract No. DE-AC02-06CH11357. Under contract No. DE-AC02-06CH11357. This work is supported in part by a Grant-in-Aid for Scientific Research Program of Japan Society for the Promotion of Science (20740161). This work is supported by the U.S. Department of Energy, Office of Nuclear Physics, under contract No. DE-AC02-06CH11357.
Towards a numerical model to constrain the time scales for vertically moving axial magma chambers beneath fast-spreading ocean ridges

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It is well accepted that AMCs (‘axial magma chamber’) under fast spreading ocean ridges are dynamic systems with the potential to oscillate vertically. Unfortunately, the time scales of these movements are poorly constrained by several multidisciplinary studies, varying between 10 and 100,000 years.

The IODP multi-cruise mission ‘Superfast Spreading Crust’ (Site 1256, equatorial East Pacific Rise), offers the possibility to study natural samples from the lower sheeted dikes from the 1256D drillcore. Detailed petrographic work led to the conclusion, that the ascent of the AMC led to the formation of ‘granoblastic dikes’ due to an intense metamorphic overprint under granulite facies conditions [1].

In this study, we apply tools of diffusion profile modeling to relictic plagioclase phenocrysts occurring in the granoblastic dikes located above the AMC. Since the plagioclases were affected by the thermal imprint of the AMC (~1200°C), the detailed analysis and modeling of the concentration profiles allows us a quantification of the residence time of the heat source (AMC) in a high position and hence, temporal information about the vertical fluctuations of the AMC can be assessed.

First estimations on the basis of CaAl-NaSi interdiffusion profiles yield average time scales of 19000 years for the development of the profiles. Calculations based on Mg concentration profiles revealed different results: The durations extracted from the profiles are much shorter in the range of ~150–400 years. This discrepancy presumably reflects different processes contributing to the development of the element distribution patterns in these plagioclase phenocrysts and its meaning has to be evaluated in the near future.


Sub-micromolar oxygen dynamics at redox boundaries of lakes

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The oxic-anoxic interface in stratified lakes is a habitat of intense microbial activity where a cascade of redox processes occurs at low O2 concentration levels. Here we report well-resolved profiles based on a two-sensor technique: The stable but slower signal from low-level optodes was verified independently with profiles from highly amplified amperometric sensors. Pre-exposure to anoxic waters reduced the drift of electrochemical sensors.

The sub-micromolar oxygen zone

An field survey of the permanently anoxic basin of Lake Zug (Switzerland) [1] revealed the spatial structure and temporal variability of the oxic-anoxic interface in the water column. The depth interval from 1 µM O2 down to the detection limit had an extension of 0.5 to 5 meters. While most profiles showed a steady decrease, several observations revealed sharp excursions due to the effect of turbulent mixing in the weakly stratified water column with a stability frequency of N2 < 10-6 s-2.

Fast fluctuations were also confirmed when sensors were deployed at constant depth. Concentrations changed by about 1 µM O2 within ~ 10 seconds and then remained quasi constant on time-scales of minutes.

The chemical gradients right at the oxic-anoxic interface were on the order of 1 mmol O2 m-3. Temperature profiles showed local maxima of >0.01°C over the sub-micromolar zone. These temperature changes were not compatible with short-term oxygen fluctuations. Therefore, the position of the oxic-anoxic interface seemed to oscillate over a limited depth range of meters. Microbial communities such as methanotrophs need to cope with oscillating conditions on the time-scale of minutes but will face a rather stable diurnal O2 supply.

The new setup will facilitate the high-resolution sampling at the redoxcline, the measurements of the in situ concentrations for important microbial reactions, and boundary conditions for more detailed reaction-transport models.

Age of the Pueblo Viejo epithermal deposit, Dominican Republic: Re-Os isotope data for sulfides from the Moore and Monte Negro deposits

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Knowledge of the age of the giant Pueblo Viejo high-sulfidation epithermal deposit (23.7 M oz Au) in the Dominican Republic is critical to our understanding of the geologic environment in which these deposits form. Two possibilities have been suggested: 1) 118-111 Ma, coeval with formation of Los Ranchos Formation island-arc tholeiites that host the deposit and represent the earliest stage of magmatism in the Greater Antilles arc, or 2) 77-62 Ma, coeval with calc-alkaline intrusions that formed during later stages of arc magmatism typical of many other deposits of this type in Cordilleran settings.

Gold is hosted directly by pyrite and to a lesser extent other sulfides, and is found in both sulfide-rich veins and layers of sulfide along bedding planes in carbonaceous shale. Analyses of six heavy mineral concentrates (largely pyrite), five vein pyrite or sphalerite and one layer pyrite from the Moore and Monte Negro ore bodies, form an isochron yielding an age of 115.1 ± 5.4 Ma with an 187Os/188Os initial value of 0.30 ± 0.14 (MSWD = 0.38). Taken separately, the concentrate analyses yield an isochron with an age of 116.4 ± 7.5 Ma and the vein analyses give an age of 116.9 ± 9.9 Ma. The combined isochron age and 187Os/188Os initial are consistent with synvolcanic derivation of metals from juvenile arc tholeiites at ca. 115 Ma.

These results confirm that high-sulfidation epithermal mineralization can form during early stages of island arc volcanism and is not confined to calc-alkaline magmatic associations, thereby considerably expanding geologic terranes that are favorable for mineral exploration.

Sea water circulation in coastal aquifers as inferred from radium isotopes: The Dead Sea case

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Saline water circulation in coastal aquifers may be a major process that controls trace element mass balances in coastal areas. This study uses radium isotopes in order to quantify lake water circulation in the Dead Sea aquifer.

The Dead Sea is extremely enriched in radium, where both 226Ra and 228Ra (140 and 1-2 dpm/L, respectively) are 3 orders of magnitude higher than in ocean water, whereas the salinity of the Dead Sea is only 10 times higher. The main sources of 226Ra and 228Ra to the lake are fresh springs and brines discharging along the lake shoreline.

Circulated Dead Sea water in the aquifer contains decreased activities of 226Ra (60 dpm/L). This coincides with the lower Ba concentrations in this water compared with the lake (1.5 and 5 mg/l, respectively). We suggest that the low 226Ra and Ba concentrations are due to precipitation of barite from the supersaturated Dead Sea water on entering the aquifer. 228Ra and the shorter-lived 224Ra and 223Ra, which have much lower activities in the Dead Sea, are enriched in the circulated Dead Sea water (20, 45 and 35 dpm/L, respectively) due to recoil and desorption. This implies that the circulation of Dead Sea water in the aquifer removes 226Ra and contributes 228Ra and 223Ra to the lake. This adds a major source with relatively high 228Ra/226Ra ratios to the Dead Sea mass balance.

In order to study the processes affecting radium isotopes in the Dead Sea aquifer, considering the dynamic conditions of the Dead Sea, we used a multi-species density-dependent groundwater flow model (SUTRA-MS). The results show that the adsorption distribution coefficient is very low, indicating that the large decrease of 226Ra in the groundwater cannot be due to adsorption, which supports the proposition that 226Ra decrease is due to precipitation of barite.

Based on 226Ra and 228Ra mass balances in the Dead Sea, the calculated amount of Dead Sea water circulation in the aquifer is 200-300 million m3/yr, which is of the same order of magnitude as all other known Dead Sea water sources at present.
Plutonium redox reactions with iron oxides under anoxic conditions

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The environmental fate of plutonium, the major transuranium actinide in nuclear waste, is largely impacted by its sorption onto and redox reactions with iron oxide minerals [1, 2] that form as corrosion products of steel in the ‘near field’ and occur widely in sediments. To obtain information on oxidation state and local structure, we reacted 242Pu as electro-lytically prepared Pu (V) or Pu (III) (1×10⁻⁵ M) under anoxic conditions in carbonate free 0.1 M NaCl with hematite, goethite, maghemite and magnetite. Pu-LIII-edge XAFS spectra were collected after 40 d and 6 months of reaction.

Results and Discussion

After reaction of either Pu (III) or Pu (V) with hematite (> 99.9 % of added Pu is sorbed on α-Fe₂O₃), Pu is mainly present as Pu (IV), with up to 30 % Pu (V). Also after reaction with goethite (γ-FeOOH) both Pu (IV) (55 %) and Pu (V) (45 %) are present. For both minerals, XAFS spectra show no strong Fe-backscattering from the substrate and also give no evidence for the formation of a solid PuO₂ phase. In contrast, EXAFS spectra of Pu reacted with maghemite (γ-Fe₂O₃) and magnetite (Fe₃O₄) are characterized by strong iron backscattering, indicating the formation of inner-sphere surface complexes. With maghemite, oxidation state mixtures of Pu (III) and Pu (IV) or Pu (IV) and Pu (V) were found while with magnetite, Pu (III) was the predominant oxidation state [3]. However, in one case and probably due to an increased Pu / magnetite surface area ratio, formation of PuO₂ after reaction of Pu (V) with magnetite was observed. These results highlight the importance of plutonium surface complexation, in addition to solid PuO₂ precipitation, in controlling environmental Pu concentrations. Further, under reducing conditions where Fe (II)-bearing oxides such as magnetite exist, it is necessary to consider trivalent in addition to tetravalent plutonium species and PuO₂ (am, hyd) for risk assessment.

Different coloured vitreous phases in obsidian

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Different coloured glass matrices obsidian are the object of the study. Their compositions and phase analyses of implemented nanocrystals were determined by Transmission Electron Microscopy (TEM). The analyses were carried out with an STEM Philips CM 200.

The Büyük Yayla obsidian (Eastern Pontides, Turkey) shows various bands, coloured black, red, and partially colourless. Moreover, a sharp black displacement (up to 1 cm) passes through the obsidian due to a still unknown shear process, displacing the several layers. Note, the different bands do not show a macroscopic 'schlieren-like' texture close to the displacement front.

The results of TEM-EDX analyses are given in the following table.

<table>
<thead>
<tr>
<th>Oxide [wt-%]</th>
<th>red glass matrix</th>
<th>colourless glass matrix</th>
<th>black glass matrix</th>
<th>glass close to the displacement trace</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2O</td>
<td>4.5</td>
<td>1.6</td>
<td>5.2</td>
<td>5.8</td>
</tr>
<tr>
<td>MgO</td>
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<td>0.2</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>Al2O3</td>
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<td>13.1</td>
<td>12.9</td>
<td>13.1</td>
</tr>
<tr>
<td>SiO2</td>
<td>76.0</td>
<td>74.9</td>
<td>74.4</td>
<td>75.0</td>
</tr>
<tr>
<td>K2O</td>
<td>4.7</td>
<td>8.4</td>
<td>5.3</td>
<td>4.6</td>
</tr>
<tr>
<td>CaO</td>
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<td>1</td>
<td>1.1</td>
</tr>
<tr>
<td>TiO2</td>
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<td>0</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>MnO</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>Fe2O3 (Fe-tot)</td>
<td>0.4</td>
<td>0.9</td>
<td>0.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 1: Chemical composition of different coloured glass matrices of the Büyük Yayla obsidian

Suprisingly the highest Fe-amount was detected in the colourless vitreous matrix. Hence, the iron solved in the glass is not responsible for the different colours of the glass. The detected 0.3 – 0.5 wt-% of hematite- and magnetite-nanocrystals colour the vitreous matrices.

Calcium and magnesium isotopes in biogenic calcite

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As shown recently [1], the isotopic fractionation of calcium is strongly correlated with the partitioning of Sr in inorganically precipitated calcite, wherein the main control on both proxies is the precipitation rate. In a follow up study [2], the inorganic correlation between Δ44/40Ca and D Sr has been verified for planktic foraminfera. We extend this approach to coccolithophores, including Emiliana huxleyi and Coccolithus braarudii, grown under controlled laboratory conditions. The slope of the regression between Δ44/40Ca (‰) and log D Sr in coccolithophores (-1.8±0.9, [3]) is within error of that in inorganically precipitated calcite (-1.9±0.3, [1]), whereas there is a large offset between the inorganic and coccolithophorid regressions due to the higher Sr content in the latter.

Comparing the fractionation of magnesium isotopes versus the Mg content in the calcitic skeletons of the Alcyonarian soft coral Rhythisma fulvum, benthic foraminifer Amphistegina sp., coccolithophores Emiliana huxleyi and Coccolithus braarudii, echinoid Echinocymus pusillus, red algea Corallina officinalis, brachiopod Terebratula sp. and sponge Acanthochaetetes wellsi, we find that species with high Mg content (>10 mol% MgCO3) have a higher degree of fractionation (Δ26/24Mg<-2 ‰) compared to low Mg species (<5 mol% MgCO3; Δ26/24Mg>-2 ‰). Planktic foraminfera and the blue mussel Mytilus edulis are exceptions with low Mg content but a high degree of fractionation (Δ26/24Mg<-3.5 ‰).

These results will be discussed in a comparative manner in terms of our understanding of the pathways of biomineralization in different calcifiers.

Post-deposition diffusion of $^{137}$Cs in lake sediments

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Large episodic emissions of radiocesium $^{137}$Cs into the atmosphere, such as those generated by nuclear weapon testing programs in the 1960s and the Chernobyl accident in 1986, have been frequently utilized when dating lake sediments. The ongoing disaster at the reactors at Fukushima, Japan, is likely to generate a new chronological marker in sediments deposited over a large part of the region that can be recognized as subsurface peak in $^{137}$Cs activities by future sedimentologists. However, the generation of a new $^{137}$Cs dating horizon in lake sediment can eliminate the use of others due to significant post-depositional mobility and catchment processes as shown in this presentation. Here we show using archived sediment samples how the $^{137}$Cs record within an annually varved sediment, from a lake situated about 1600 km from Chernobyl, is successively altered between 1985 to 2007 due to Chernobyl fallout and subsequent post-depositional diffusion and catchment inputs. The record reveals how Chernobyl $^{137}$Cs becomes incorporated into the summer sediment in 1986 and diffuses downward in the core at a decreasing rate over time, making the marker of 1964 originally present in the core sampled three weeks before the Chernobyl accident unrecognizable two years after the accident. It is, therefore, questionable whether $^{137}$Cs peaks in deep sediment can be used to recognize sediment deposited in the 1960s in regions that has received significant fallout from the accidents in Chernobyl or Fukushima.

Atomic force microscopy study of the dissolution of a calcite surface in the presence of phosphate ions

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The dissolution of calcite in the presence of phosphate solutions has been studied using Atomic Force Microscopy (AFM). The presence of phosphate in aqueous solutions is known to inhibit calcite growth [1] and has been successfully used to reduce limescale formation. In this study, solutions containing phosphate salts such as ammonium and sodium phosphate were studied in order to compare their influence on the dissolution of a calcite surface (10-14) during continuous flow in the fluid cell of an AFM.

In the presence of phosphate solutions at pH $\sim$ 8, a significant decrease in the dissolution rate was observed. However, the etch pit density, increased for both ammonium and sodium phosphate salts, suggesting a kosmotrope hydration character of phosphate ions and therefore similar behaviour to that of fluorine ions on calcite dissolution [2]. It was also observed that the dissolving calcite surface can act as a structurally suitable substrate for calcium phosphate growth, which may prove to be an environmentally important mineral replacement reaction for remediation of phosphate rich systems.

Figure 1: AFM image of calcium phosphate growth on a calcite cleavage surface. The process is limited by the release of $\text{Ca}^{2+}$ from the dissolution of calcite.

Origin of the nodules in the 18.6 ka Sarno plinian eruption of Mt. Somma-Vesuvius (Italy) and their significance

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Nodules (coarse-grain 'plutonic' rocks) were collected from the phreato-magmatic phase of the Sarno eruption in C. Traianello quarry, located on the NE slope of Mt. Somma. Based on the mineral composition the rocks can be classified as monzonite-monzogabbro. They consist of An-rich plagioclase, K-feldspar, clinopyroxene (ferro-diopside), mica (phlogopite-biotite) ± olivine and amphibole. Unlike most of the nodules from the other eruptions, these samples do not have typical cumulative texture, but rather display a porphyrogranular texture. The phenocrysts are large (up to few mm) with variable compositional zoning. The phenocrysts are often partially to completely enclosed by later poikilitic feldspars. Sometimes irregular intergrowths of alkali feldspar and plagioclase and smaller unidentified crystals can be observed. These features are interpreted as crystallized melt pockets. Based on their textures, the nodules may represent the in situ crystallizing melt on the walls of the magma chamber. The lack of the interstitial glass, which is common in nodules from similar environments, can be explained by the time difference between the plinian and the phreatomagmatic phase. The time difference might have provided sufficient time for the interstitial melt in Sarno samples to crystallize.

Minerals, especially clinopyroxenes, are abundant in crystallized silicate melt inclusions. The inclusions consist of mica, oxide minerals, clinopyroxene and possibly apatite, feldspar, interstitial glass, bubble. Unlike nodules from other eruptions, all fluid inclusions in Sarno samples are single phase and secondary in origin, and not associated with melt inclusions. The different textures and inclusion populations may indicate different pre-eruptive conditions and processes, compared to other eruptions. Melt inclusions in clinopyroxenes have been analyzed by LA-ICP-MS. The major and trace element compositions of MI are similar to the products erupted during the plinian phase, indicating that they may be co-genetic. Melt inclusions have been rehomogenized for further analyses to determine the volatile content, in order to estimate a minimum crystallization depth.

Monte Carlo study of aggregation of alkyltrimethylammonium ions at the montmorillonite-water interface

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Unlike naturally occurring bentonites, organically modified clays as well as the mechanisms determining their observed adsorption properties are still not well understood. To establish a relation between experimental observations and underlying molecular structures, we performed classical molecular simulations of the external montmorillonite surface modified by alkyltrimethylammonium (C_nTMA^+, with n being the number of methyl (ene) groups in the alkyl chain). The adsorption of alkyltrimethylammonium ions at the montmorillonite-water interface and the formation of interfacial C_nTMA^+ aggregates at higher concentrations of adsorbed C_nTMA^+ were studied. The simulations were performed in NVT-ensemble at a temperature of 298 K applying the Metropolis and the configurational-bias Monte Carlo algorithms for increasing surface concentrations of C_8TMA^+, C_12TMA^+, and C_16TMA^+ ions. The discussion will comprise the arrangement of adsorbed organic and inorganic ions, structure and type of adsorption complexes, conformation of alkyl chains, and the water structure at the organically modified montmorillonite-water interface taking into account findings of previous experimental and simulation studies.

Mineralological Magazine www.minersoc.org
Dolomitization of serpentinized harzburgite from the Atlantis Massif

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Ophiocarbonate breccias consisting of fragments of serpentinized peridotite and carbonate cement have been reported from outcrops at the Atlantis Massif, MAR1. While the carbonate cement precipitates due to mixing of high-pH, Ca-rich serpentinization fluids with seawater, the direct replacement of serpentinite by dolomite is more difficult to explain. Here, I report on observations made in a dolomite-altered, strongly serpentinized, partly steatitized harzburgite, from the IODP Leg 304, Hole 1309B at the Atlantis Massif. Dolomite appears in mesh and hourglass texture of completely serpentinized olivine adjacent to a talc-tremolite altered shear zone. The dolomite in these samples is surrounded by a zone of serpentine (Mg# 98), and magnetite, which traces the former (sub-) grain boundaries of olivine. Orthopyroxene is partly serpentinized to bastite, which subsequently underwent partial steatitization but not dolomitization. Both clinopyroxene and Cr-spinel are unaltered.

Dolomite in serpentinite can form by conductive heating of seawater2; however, in samples from Hole 1309B petrographic observations and microprobe analyses suggest a direct replacement of brucite and serpentine by dolomite. Phase relations in the system MgO-CaO-SiO2-H2O-CO2 indicate that brucite is the first mineral being replaced by dolomite at relatively low CO2aq activities, while dolomitization of serpentine and talc requires higher CO2aq activities. However, it remains to be resolved whether the CO2 is of magmatic or of seawater origin. The Mg needed for the formation of dolomite is likely contributed by brucite and/or serpentinite themselves, whereas Ca may have been transported from the adjacent talc-tremolite shear zone. Alternatively, the Ca may have been contributed by the dissolution of the Ca-Tschermaks component of partly serpentinized orthopyroxene.

This pilot study indicates that serpentine and brucite can act as a sink for CO2 in the oceanic lithosphere, in particular where seawater and/or magmatic fluids interact with hybrid mafic/ultramafic lithologies.


Chromium mobility in hydrous fluids at upper mantle conditions

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Chromium is a minor component in the earth's mantle and is considered to be immobile in aqueous fluid under crustal and most mantle conditions. Exceptions to this are for example K-rich diamond forming fluids, shown to contain up to 1 wt% Cr2O3 (on a volatile free basis). A series of high-P experiments on the solubility of Cr2O3 in KCl bearing water were done using rocking multi anvil diamond trap techniques (1000 and 1200 °C; 4 and 6 GPa) combined with cryogenic LA-ICP-MS in order to determine Cr mobility in saline fluids (e.g. diamond forming fluids) under mantle conditions and its possible involvement in deep metasomatism. Chromium solubility in KCl-bearing water increases with salinity (KCl). At 250 µg/g KCl, Cr solubility in water is between 100 and 200 µg/g, independent of pressure. At 4 GPa, an order of magnitude increase in Cr-solubility is observed only for the 3 wt% KCl solution, while at 6 GPa such increase is observed already at 1.3 wt% KCl. No significant effect of temperature is observed. Metasomatic Cr-rich mineral assemblages are encountered in both subduction zone and deep lithospheric mantle environments, where alkali-rich hydrous fluids, similar to those examined in this research, are regarded as major metasomatic agents. In some cases, unique minerals found as micro- and macro- inclusions within diamonds (e.g. chromite and phlogopite) have significantly different compositions than common mantle minerals and are much richer in Cr. Thus, saline hydrous fluids can be considered an important metasomatic agent at deep lithospheric mantle conditions and appear to be efficient in transporting elements such as Cr during rock water interaction.
Evidence of K-Fe metasomatism in the SW Scottish Highlands

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Metamorphosed basaltic lava flows, tuffs, sills and dykes are emplaced within metasedimentary rocks which are part of the Dalradian Supergroup (Argyll Group) in the SW Scottish Highlands [1]. These metabasaltic sills were affected by at least three fluid-rock interaction events during greenschist facies regional metamorphism: pre-metamorphic spilitisation, syn-metamorphic carbonation of metabasaltic sills and post-metamorphic quartz-carbonate-sulphide veins [2]. The infiltration of H2O-CO2 fluids during carbonation led to a mineral assemblage zonation within the metabasalt with carbonate-free interiors and carbonate-rich margins [3].

These three fluid events and an additional K-Fe metasomatic event of uncertain timing could be identified in altered metabasalt on the island of Islay in the SW Scottish Highlands. At this locality, the altered metabasaltic sills display a distinct change in mineral assemblage which seems to be coupled to brittle to ductile faulting. Only the areas close to the fault seem to be affected by the K-Fe metasomatism. The mineral assemblage pl+zo+ich+qtz+c changes into ep+chi+qtz+cc+ht+bt towards the fault system which cuts through the outcrop. These results were achieved by petrographic analysis, point counting of 1000 evenly spaced points in selected thin sections, XRF and SEM analyses.

The fact, that hematization took place and zoisite changes into the more Fe-bearing epidote, suggests that iron was added during the fluid event. The formation of biotite leads to the assumption that K-metasomatism is also coupled by this fluid-rock interaction.

Is it possible to constrain a sequence of fluid events in this area? The hematite phenocrysts are only slightly affected by the foliation of the metabasalt which suggests that the K-Fe metasomatism occurred after peak metamorphism (400-550°C, 10 kbar) [3]. Also its spatial association with faulting suggests that K-Fe metasomatism was occurred late during the fluid-infiltration history.


Hf-W chronometry of angrites: Implications for 26Al heterogeneity and core formation in protoplanets

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Angrites formed by some of the earliest igneous activity in the solar system and provide insights into the early stages of planetary melting and differentiation. Moreover, they are pivotal reference points for early solar system chronology [e.g. 1-3]. In order to study the processes and timescales of metal segregation in early protoplanets and to assess the distribution of short-lived radionuclides in the early solar system, the 182Hf-182W system was applied to a comprehensive suite of angrites. 182Hf-182W isochron ages for angrites are in excellent agreement with previously reported 206Pb-206Pb and 26Mg-26Mg chronometries [e.g. 2]. These inconsistencies are best explained by a heterogeneous distribution of 26Al in the early solar system, suggesting that at the time of CAI formation the angrite precursor material had an 26Al/27Al of ~1.8 x 10^-5, substantially lower than values commonly measured for CAI. Based on the Hf-W results four texturally and temporally resolved groups of angrites can be identified that were derived from at least two distinct mantle sources. These mantle sources are the result of separate events of core formation, both of which took place within ~2 Myr of CAI formation. Thus, core formation in the angrite parent body did not occur as a single event of metal segregation from a global magma ocean but rather took place under varying conditions by several more local events. Heterogeneities in the Hf-W systematics of the two distinct angrite source regions may result from efficient core formation in some areas of the angrite parent body or may reflect variable redox conditions during metal segregation. The absence of global melting and homogenization in spite of an early accretion is consistent with a relatively low initial 26Al/27Al inferred here for the angrite precursor material.

Geodynamic implications of new U-Pb zircon ages for the Kamanjab Inlier (NW-Namibia)

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The Huab Metamorphic Complex (HMC) and Fransfontein Granitoid suite (FFG) are part of the Kamanjab Inlier (KI) in NW-Namibia. It is a poorly known pre-Pan African basement complex and, together with the Epupa complex (EC) further NW and the Grootfontein complex (GC) further E, marks the SW-margin of the Congo craton in N-Namibia. New LA-ICPMS U-Pb zircon ages frame FFG emplacement to 1.88-1.83Ga and protolith ages for HMC orthogneisses to 1.86-1.83Ga. These ages are roughly 100 m.y. older than protolith ages from the northern EC close to the Angolan border and roughly 100 m.y. younger than the GC. The southern EC in the Hoanib area is the only known Archean basement in Namibia, but shows eNd (1.83Ga) of -10.9 to -6.5 compared to those of the northern EC (-2 to 4.2), FFG (-5.9 to 1.2) and HMC (-2.3 to 2.3). Our study supports earlier speculations that the southern EC is an exotic terrane within the Namibian basement complexes. In contrast, the KI is comparable to the northern EC and GC and geochemical data indicate an active continental margin setting. This points to an event of Paleoproterozoic crustal growth at the SW border of the Congo Craton starting in the present E gradually moving towards the present NW.

The garnet-spinel transition in fertile and depleted mantle: Experimental data, thermodynamic calculations and implications for magmatic processes

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With increasing depths in the Earth’s mantle, the aluminous phase in the upper mantle changes from plagioclase to spinel to garnet. The transition from spinel lherzolite to garnet lherzolite could potentially influence the characteristics of some kinds of basalts, particularly mid-ocean ridge basalts (MORB), since this transition is thought to occur at about the same depths at which MORB may originate. Several studies have investigated the transition from garnet lherzolite to spinel lherzolite in simple systems (e.g. CaO-MgO-Al2O3-SiO2) (e.g. [1-3]) but, due to experimental problems associated with slow reaction rates, few studies have tried to experimentally investigate the garnet-spinel transition in more complex and depleted composition (e.g. [4-5]). Here we set out to investigate phase relations from fertile to depleted mantle compositions using a new set of thermodynamic data and free energy minimization techniques [6]. We show that the stability fields of garnet and spinel in upper mantle lithosphere critically depend on the bulk composition of the peridotite. In fertile bulk compositions, the transition from spinel to garnet-bearing rocks is relatively sharp but in depleted bulk compositions there is a large pressure-temperature field where garnet and spinel coexist. We will show that the garnet-in reaction in depleted peridotite occurs in much greater depths than in fertile lherzolite. Furthermore, the results in depleted compositions may also be of relevance for the diamond exploration industry as the calculated Cr-rich spinel and garnet compositions may be used to quantitatively estimate pressures of origin and therefore evaluate the so-called diamond potential of mineral concentrates [7].

Secondary minerals in mine wastes at Sb deposits in Slovakia

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In this work, we have summarized results from a detailed mineralogical study of the weathering products formed in the environment of tailing ponds and soils from five Sb deposits in Slovakia, based on 250 samples of flotating tailing materials and soils, 2500 electron microprobe analyses and 500 micro-X-ray diffraction (µ-XRD) analyses. All studied bulk samples are rich in Fe (24.2–181 g/kg), As (0.1–13.5 g/kg), and Sb (1.2–15.7 g/kg). The most frequent sulphides in the flotation wastes are pyrite (FeS2) and arsenopyrite (FeAsS); stibnite (Sb2S3) is rare owing to its rapid oxidation.

The most common Sb-bearing secondary oxide is tripuhyite (FeSbO4) with variable Sb (15.94–50.83 wt. %) and Fe content (4.13–41.52 wt. %). Unit cell volume is in the range from 64.70 Å3 to 75.83 Å3 and depends mostly on the Fe/(Fe+Sb) ratio of the tripuhyite grains. In the tailings and soils rich in Ca, secondary minerals with the pyrochlore structure have been identified. These phases are rich in Sb (up to 52.90 wt. %), Fe (up to 21.22 wt. %) and Ca (up to 7.40 wt. %) and the µ-XRD patterns fit well with the structural models of stibiconite (Sb6+2Sb5+2O12(OH)) and lewisite (Ca, Fe2+, Na)2(Sb, Ti)2O7). The most frequent secondary mineral at all studied sites is goethite (α-FeOOH), with high content of Sb (up to 14.49 wt. %) and As (up to 6.49 wt. %). Cell parameters depend on incorporation of foreign elements, in agreement with earlier studies. Frequent are also X-ray amorphous Fe oxides with variable amounts of adsorbed elements (up to 6.66 wt. % of Mg, 13.91 wt. % of Sb and 10.64 wt. % of As). Simple secondary Sb oxides such as cervantite (Σ6SbO2) and seframontite (Σ3SbO2) were observed each just in one soil sample. The most common product of arsenopyrite oxidation - scorodite (FeAsO4·2H2O) occurs rarely. Beudantite (PbFe3(AsO4)(SO4)(OH)) was identified in a few samples with increased content of Pb. In one sample, a porous secondary oxide rich in Pb and As was identified by µ-XRD as clinomimetite (Pb2(AsO4)3Cl).

This work was supported by Slovak Research and Development Agency under the contract No. VMSP-P-0115-09.

Experimental constraints on the composition of slab liquids below arc volcanoes

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The flux of elements from the slab into the mantle wedge is governed by the composition of the different subducted lithologies, the partitioning behaviour of trace elements and the subduction geotherm. Recently it has been shown that the concentration of key elements such as K, Zr, Ti, Nb and REE depends primarily on T and is controlled by the solubility of accessory phases, such as phengite, zircon, rutile and allanite, in the melt [1, 2]. This T-concentration relationship can be used as a geothermometer to determine the top slab T in subduction zones and suggests values that vary from 750 to 950 °C for different subduction zones [3]. Crucial questions that remain open are the effect of pressure and the presence of additional volatiles such as S, Cl and F on the stability of accessory phases and the composition of slab liquids.

Here we report preliminary results on crystallisation experiments on a H2O-saturated and trace element-doped MORB composition at 5 GPa and 750-1000 °C. Together with previous results at 2.5 GPa and 750-900°C [2] the experimental dataset now covers the full range of P-T conditions predicted for the slab below volcanic arcs. The dataset will be augmented with a few runs containing additional S and F.

First results show that at 5 GPa the wet solidus of basalt is <900 °C. Experimental melts at 5 GPa are granitic compared to trondhjemitic melts at 2.5 GPa. With increasing P, DNa in cpx increases and hence Na/K in the melt decreases. All runs contain gt, cpx and rutile. Allanite is present up to 950 °C. No effect of P on allanite composition has been recognised so far. Coesite is found to be stable at P >5 GPa. The trace element contents of the glasses are currently investigated by LA-ICPMS. One run at 950 °C and 5 GPa, containing small quantities of F, crystallised REE-bearing CaF2 and allanite. From these preliminary results we anticipate that a) increasing P (increasing depth of the slab) can explain the change from Na-rich to more K-rich signal in arc magmas and thus K is not only controlled by phengite stability and b) addition of F in the fluid stabilises REE-bearing CaF2 in the solid residue.

Translocation of synthetic inorganic nanoparticles in a water-saturated sediment column

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Breakthrough of synthetic, inorganic nanoparticles (NP) in porous media observed in laboratory experiments [1] raises the assumption of NP posing a risk to drinking water treatment methods [2] such as riverbank filtration. Hence, the aim of this experiment was (i) to gain first hints on the fate of NP under near-natural conditions and (ii) to understand the processes of NP interactions taking place in the water phase and the sediment.

Four types of NP (TiO2, Ag(0), CeO2, Sb2O5) were suspended in the supernatant of a water-saturated sediment column (1 m length) implemented into a slow sand filtration pond. The column was filled with coarse-grained medium sand and was fed with surface water (pH 7, 8, I = 19 mM, turbidity = 3 FNU) from the surrounding pond. The column was sampled in various depths (20 cm, 40 cm, 60 cm, 80 cm) and at the outflow. The NP were fractionated by filtration (0.45 µm and 0.1 µm) and the respective analytes (Ti, Ag, Ce, Sb) were determined using ICP-MS.

In the water phase, NP concentrations were reduced by a factor of 1000 due to particle aggregation, which was predominantly caused by an increase in ionic strength in relation to the original NP suspension. This resulted in a shift of the particle size distribution towards larger sizes and NP were found to form hetero-aggregates with suspended particulate matter. Our observations demonstrate that hydrochemical conditions substantially affect size distribution and aggregation of the investigated NP.

In the sediment, Sb2O5, the NP with the most negative zeta potential, was the only NP showing breakthrough (up to a depth of 40 cm). This result confirms that the zeta potential is a key factor in NP suspension stability. The various conditions led to a change in particle size distribution during sediment passage, too. The processes which play a key role in NP translocation remain to be elucidated.

Pentose sugars are major biochemical building blocks. Prebiotic syntheses have been proposed leading to complex mixtures including 4-, 5-, and 6-carbon sugars [1, 2]. However, the pentose sugar D-ribose has the greatest biological importance because it is the sugar found within modern nucleic acids. We are investigating whether this is due to some exceptional characteristic of ribose associated with its interaction with mineral surfaces.

Recent study of the adsorption of nucleosides and nucleotides on rutile [3] indicates that adjacent OH-groups on the ribose part of these molecules play a critical role in the attachment to mineral surfaces. The four pentose sugars ribose, xylose, lyxose and arabinose differ only in the arrangement of the OH-groups and their stereochemistry in solution. This suggests that the different structures of these sugars might lead to selective adsorption on mineral surfaces.

The present study is focused on interactions of D-ribose and D-xylose on rutile (α-TiO2, pH_PZC = 5.4, BET = 18.1 m²/g) in 10 and 100 mM NaCl solutions over a wide range of pH conditions (3-10). The rutile powder is the same as previously used for amino acid adsorption studies [4]. Batch adsorption experiments of the two sugars individually and in mixtures indicate that adsorption of both sugars increases with increasing pH of the solution. The pH dependency of adsorption is more pronounced for ribose leading to a difference of ~20% adsorbed at pH > 8.5. Our preliminary results indicate a significant difference in the adsorption behavior of the two sugars.

Controls on lignin degradation in a temperate deciduous forest

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Degradation of lignin might play a critical role for carbon (C) storage in soils. Changes in climate or land-use affect inputs of nitrogen (N) and dissolved organic matter (DOM) to topsoils. We studied possible consequences for lignin degradation at a beech–oak site in Southern Germany. We hypothesized that degradation of lignin and other recalcitrant organic matter (OM) decreases with N inputs, but increases with input of easily degradable OM. The study also addressed effects of DOM composition on lignin degradation.

A column experiment using A horizon samples was conducted. Solutions differing in N and of different concentrations of DOM of various composition (i.e. glucose, DOM extracts of fresh or humified litter material) were added every 2-4 weeks for 11 months. Total N additions ranged from 0-32 mg N g-1 soil-N, organic C additions were 0 or 11 mg C g-1 soil-C (i.e. maximum C and N added equaled 2-3 times the annual input of dissolved organic C and total N from forest floors). Lignin degradation was assessed after 5 and 11 months using the CuO oxidation method.

In controls (no N or DOM added), the cummulated CO2-C evolution (during 11 months of incubation) amounted to 13% of initial soil-C, while CO2-evolution diminished during incubation indicating decreased C availability. Yields of lignin phenols decreased by 19% (0-11 months). Even in the later period (5-11 months), lignin degradation proceeded, suggesting it was not limited by easily degradable OM. In line, glucose addition increased CO2 evolution from soil-OM, but lignin degradation was not affected. However, addition of DOM led to enhanced lignin oxidation after 11 incubation months but the composition of DOM had no effect. This suggests that lignin degraders were stimulated by input of a complex mixture of organic compounds, but against expectations the share of easily degradable compounds played no role. Also N input did not affect CO2 evolution or lignin degradation. To conclude, altered N inputs to topsoils due to land-use or climate change will not affect lignin degradation, whereas altered DOM inputs presumably has an effect. However, altered C availability seems not to be the reason. Other possible mechanisms will be discussed.

Basanite-phonolite mixing indicated by trace elements in green-core clinopyroxenes from La Palma

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Green-core clinopyroxenes (Cpx) are ubiquitous in alkaline basalts worldwide. Commonly, anhedral and rounded cores are enriched in Na, Fe and Mn compared to brownish rims and groundmass Cpx. Most are believed to have been formed by crystallization in evolved melts followed by magma mixing prior to eruption [1, 2].

This interpretation was tested by trace element analyses of Cpx phenocrysts in lavas from the active Cumbre Vieja volcano on La Palma (Canary Islands) where basanites and tephrites contain abundant green-core Cpx. Zoned and unzoned greenish Cpx in phonolites show a wide compositional range and characteristic S-shaped REE spectra with (La/Nd)N >1, (La/Lu)N >1 and (Tm/Lu)N ≤1. The spectra strongly differ from those of brownish Cpx rims and Cpx phenocrysts in basalts to tephrites, that have (La/Nd)N <1 and (Tm/Lu)N >1. The latter are also more restricted in composition and have higher compatible and lower incompatible trace element contents, and lower Zr/Hf and Nb/Ta, than phonolite-hosted Cpx. Calculated REE spectra of corresponding melts show strong enrichment of light relative to heavy REE, and are straight for basalts to tephrites but concave-upward for phonolites. All these differences are consistent with fractionation of observed phenocryst phases during the formation of phonolitic melts, with titanite being responsible for Nb/Ta fractionation.

Trace-element compositions of rounded cores from green-core Cpx overlap completely with green Cpx in phonolites, but differ systematically from brownish Cpx. This provides unequivocal evidence for formation of green-core Cpx in phonolitic melts, resorption after mixing with more primitive melt, and subsequent overgrowth by brownish Cpx. Mixing most likely occurs in the uppermost mantle at 430-780 MPa where La Palma magmas fractionate prior to eruption [3]. The commonness of green-core Cpx shows that mixing between basanitic and phonolitic melts periodically occurs beneath La Palma and is important to the evolution of magmas. The data also suggest that much more phonolite is produced at depth than inferred from erupted lavas.

**Fluid evolution in the Byngi gold deposit, central Urals, Russia**

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The Byngi gold deposit, located in the central Urals, consists of multiple quartz veins that occur in and above the apical part of a buried plagiogranite stock that is part of a gabbro-granitic complex. The volcanicogenic country rocks that host the quartz veins have undergone metasomatic alteration that is associated with gold mineralization. Stock has been dated at 345-318 Ma.

The studied sample is vein quartz containing pyrite and chalcopyrite. Gold is closely associated with chalcopyrite. The ore minerals fill cracks in quartz, suggesting mineralization is later than at least some of the quartz. Pyrite shows two (or more) generations – the earliest is growth of idiomorphic crystals that trapped chalcopyrite and grains of quartz inside. The second generation represents metasomatic growth of pyrite over the earlier pyrite. A later event produced fractures between the two generations of pyrite, and these were later filled by quartz and chalcopyrite. The final stage is represented by deformation of ore minerals. The sample thus contains three generations of quartz: early recrystallized quartz formed before ore minerals, quartz (± chalcopyrite) in cavities within pyrite, and finally quartz precipitated in later brecciated pyrite.

Fluid inclusion assemblages (FIAs) were measured from the earliest and latest stage quartz using a Linkam THMS-600 heating/cooling stage, Raman spectroscopy and cathodoluminescence. All FIA contain inclusions that contain an aqueous liquid phase and liquid/vapor CO2 and contain about 10-20 mole% CO2. CO2 melts in the range -57.1 to -58.9°C, suggesting the presence of other volatiles, but no other gases were detected by Raman analysis. Salinity calculated from the melting temperature of clathrate [1] ranged from 1 to 9 wt% NaCl equivalent. Homogenization of the CO2 phase ranged from 10.5-30.1°C. FI in early quartz homogenize at 110-145°C, those in intermediate quartz at 130-145°C, and the latest quartz at 200-240°C.


**Differences in coupling between AOM and SRR in marine sediments**

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Microbially mediated anaerobic oxidation of methane (AOM) is a major methane sink in the ocean, coupled to bacterial sulfate reduction (SRR) as electron accepting process. Yet, with increasing data of AOM and SRR measured in various sedimentary environments, ranging from cold seeps to diffusion dominated habitats, the regulation and linking of both processes remains controversial. In order to investigate if the regulation of AOM and the coupling between AOM and SRR is consistent in all environments, sediment from diffusion dominated sites on the continental shelf (Aarhus Bay and Kattegat/ Denmark) and a methane seep (Black Sea) were incubated under different combinations of methane and sulfate concentrations, and the response of both AOM and SRR evaluated. The experiments confirmed the strong dependence of AOM rates on methane concentrations at all sites but demonstrated differences in sulfate reduction rates with increasing concentrations of both, methane and sulfate. Whereas a close coupling of AOM and SRR, and respectively a strong dependence of rates on both substrates, was evident at the methane seep, the rate measurements from Aarhus Bay provide direct evidence for a decoupling of both processes. Furthermore, the ratio of both rates deviated from the even stoichiometry observed at the methane seep. The experiments demonstrate that there are significant differences in the regulation and coupling of AOM rates and SRR at different sites indicating that AOM might not be mediated in the same way at all sites.
Paleoenvironmental evolution of the Lower Miocene organic clays (the Sokolov Basin, Eger Graben, Czech Republic): Inorganic proxies

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Lacustrine sediments of the Cypris Formation cover in the Sokolov Basin approximately 20 km² of its area being represented chiefly by offshore organic matter and pyrite-rich clays of a thickness ranging from 130 m to 180 m, whereas nearshore facies are missing or preserved only rarely. Variations in Fe, Ca, K, Rh, S, Sr, Ti and Zr contents in lacustrine clays were studied in drill core (Dp 333-2009) using a portable XRF spectrometer Innov-X Alpha. The results of XRF measurements were verified by ICP-MS method after total digest of samples. The constant Ti/Zr ratio in the entire clay sequence indicates a uniform source of terrigeneous material brought into depositional area during the whole sedimentation period. Similarly, the Fe/Zr and Fe/Ti ratios are invariable thus indicating that most of the iron is confined to terrigenous material. Therefore, the correlation between Fe and S in clay is insignificant. The K/Zr and Rb/Zr ratios gradually increase from the bottom to the top of the studied sequence documenting an increase in the content of clay minerals in the sediments studied. Increase in Ca/Zr and Sr/Zr ratios upward in the section is attributed to the rising content of carbonates. The progressive increase in the content of clay minerals and carbonates towards the top of the sequence studied has been interpreted as indicating a gradual transition from the hydrologically open, relatively deep, freshwater lake environment, to the hydrologically closed, shallow water alkaline lake environment. This interpretation corresponds with the increasing content of anhydrite, montmorillonite and analcime upward in the clay sequence. Lacustrine clays of the Cypris Formation are usually laminated. The K/Zr and Rb/Zr ratios in organic matter-rich (10–18% TOC) and organic matter-poor (2–10% TOC) laminas are basically the same, but the Ca/Zr and Sr/Zr ratios are significantly higher in organic matter-poor laminas. Therefore, it is believed that the lamination reflects most likely seasonal variations in the organic matter and carbonate deposition.

This study was supported by the Grant Agency of the Czech Republic (GAČR 205/09/1162).

Modelling global trace gas emissions from biomass burning: Importance of emissions models vs. observed burned area

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Biomass burning is one of the largest sources of atmospheric traces gases and aerosols globally. Emissions from biomass burning can be quantified by a combination of observed burned area, terrestrial ecosystem models to simulate fuel loads and the effect of fire on ecosystem dynamics, and emission factors that relate combusted biomass to the emission of various trace gases. However, different versions of global burned area data derived from satellite observations and emissions models still show major discrepancies. Studies on burned area products have so far focused on product inter-comparison, while the consequences of those discrepancies for fuel simulations and emissions modelling with ecosystem models are still unknown.

Here, we perform a sensitivity analysis of the influence of burned area products and emissions models using the ecosystem model LPJ-GUESS and modified version of the global fire model Spitfire. The emissions model follows two different strategies: a conventional one where fixed emission factors are multiplied by biomass combusted, and an alternative one where combustion efficiency depends on the ratio of grass to total combusted litter. Aerosol particle mass is also computed, following two different approaches derived.
Geochemical characterization of biosignatures in subseafloor basalts

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The discoveries of intriguing tubular and granular alteration features in subseafloor basalt glasses, ophiolites, and ancient greenstones [1, 2] has exciting implications for increasing our understanding of global geochemical cycling and the evolution of life on Earth, as well as for exploring other planets for signs of life. The suggestion that these features could represent some of the oldest signs of life on Earth [3] has sparked debate about their putative biogenicity. We have been working to constrain the physical and chemical conditions within the basalts at the time of alteration in order to put together a model of the mechanisms of alteration and preservation of the features.

Using a number of synchrotron-based X-ray microprobe and microspectroscopy techniques we have been able to geochemically characterize these alteration features at the sub-micron scale. We have mapped both major and trace element distributions in numerous tubular and granular alteration features, which shows intriguing patterns of mineral dissolution and authigenic precipitation. In addition, we have collected micro-diffraction patterns and analyzed the oxidation and coordination states of major and trace elements in potential biominerals, which may have formed as a result of microbial metabolic processes. We have been able to show that the mechanism of formation of the tubules clearly involves initial dissolution of the glass, followed by precipitation of authigenic minerals, with concomitant partial to complete oxidation of the reduced metals, such as Fe and sometimes Mn. XANES analyses have also revealed the coordination chemistries of these metals, leading to the identification of target phases that are potential biominerals.


The study on arsenic stabilization using recycled mine sludge

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Materials and methods

The stabilization efficiencies of arsenic (As) in contaminated soil were evaluated using mine sludge collected from an acid mine drainage (AMD) treatment system. The soil samples were collected from the Chungyang area, where abandoned Au-Ag mines are located in South Korea. As (V) and As (III) sorption properties were investigated to evaluate the As sorption capacity of mine sludge. The stabilization experiments of As in soil carried out various ratio of mine sludge.

Results and discussion

The pH of the soil samples was 5.07, and the soil texture was silt loam (sand 33%, silt 63%, clay 4%). The CEC value and LOI were 19.8 meq/100 g and 25.6%, respectively. From the results of the SPLP and TCLP tests, the arsenic concentrations in the studied soil were 0.23 and 1.14 mg/kg, respectively. These results show a lower value for the TCLP than that proposed by the USEPA (5 mg/kg). The total arsenic concentration via aqua regia digestion of the soil was 145 mg/kg.

In the kinetic experiments, 99% of As (V) was removed within 3 min and 20% of As (III) was removed from the solution after 20 min and 98% within 12 hours. As (V) and As (III) adsorption process is not pH dependent, and the adsorption isotherm of As (V) and As (III) followed Langmuir isotherm model.

The pH variation depends on the mine sludge ratio (0, 0.5, 3 and 5 wt%) to total soil weight in As stabilization experiments. The extracted arsenic concentrations increased in the control experimental set. The average As concentration was 2.8 μg/L at the 0.5 wt% mine sludge mixed set, and 1.3 μg/L of As was extracted from both 3 and 5 wt% experimental sets. These results suggested that mine sludge influenced on As stabilization and 3 wt% of mine sludge suitable for stabilization of As in soil.
Predicting spatial and temporal concentrations of arsenic within the Mekong Delta

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It is generally accepted that arsenic release from sediments within the vast deltaic plains of South and Southeast Asia transpires under reducing conditions, and microbiologically-mediated reductive dissolution of arsenic-bearing iron (hydr)oxides is the dominant reaction liberating arsenic to the aqueous phase. Further, strong links have been established between groundwater contamination and arsenic release within near and subsurface environments, and it has become clear that hydrogeologic conditions impart a dominating effect on As distribution during and following liberation. The hydrologic systems of the deltaic aquifers throughout South and Southeast Asia, however, have drastically changed due to extensive groundwater extraction, and from massive anthropogenic alteration of the soil-sediment profile for numerous small and large-scale (excavation) projects. We here present a unifying biogeochemical-hydrogeologic analysis of processes governing arsenic using field-calibrated one- and two-dimensional reactive transport simulations, and utilize three-dimensional simulations to examine the possible effects of excavation and irrigation pumping—processes prevalent in other countries in South and Southeast Asia. The ability to project arsenic levels in space provides the critical capacity to assess optimal locations and depths for groundwater extraction—provided they exist—while projecting temporal changes allows us to determine long- and short-term threats to low-arsenic wells, particularly those arising from land use changes.

Arsenic mobility in a waste rock pile at Dlouhá Ves, Czech Republic

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Products of fifty-years long alteration of a waste rock pile from a Pb, Zn-deposit at Dlouhá Ves, Vysočina region, Czech Republic, were studied in the pile centre (profile I) and on its slope (profile II). The pile material had initially high sulphide (10-20 wt. %) and very low carbonate content (1-2 wt. %); the only primary mineral of As was arsenopyrite.

Significant oxidation of sulphides (pyrite, pyrrhotite, arsenopyrite, sphalerite, galenite) took place in both profiles. The principal As-bearing phase at the top of the profile I is goethite, while down to its base most of As is present in the jarosite group minerals. Melanterite and anglesite were found in a sulfide-rich, lower part of the profile I. At the profile II, minerals of the jarosite-beudantite group, scorodite and kañikite prevail and no Fe (II)-minerals were found. The paste pH was lower at the profile I (31.9) than at the profile II (32.8). Processes in the pile are affected by the ratio pyrite to arsenopyrite, where high pyrite content decreases the As/S ratio and results in the formation of jarosite group minerals and low pH conditions. Where arsenopyrite predominates, sulphides are coated by scorodite and other Fe-As phases like schwertmannite, which limit their further oxidation.

Arsenic concentrations released during the leaching experiments were generally low; maximum amounts (up to 0.56 ppm) were released from horizons with jarosite and arsenopyrite. In contrast, minimum amounts of arsenic were released from horizons with beudantite and scorodite. Differences between both profiles are caused mainly by limited water flow through the pile material and also limited penetration of oxygen into the deep parts of the excavation profile. It seems that beudantite and scorodite could represent a long-term option for immobilization of arsenic, but arsenic stored in jarosite can be mobilized relatively easily [1, 2]. However, potential mineralogical transformations and stability of arsenic in beudantite group minerals have yet to be evaluated, because the long-term stability of secondary arsenic minerals remains a serious problem [3].


Mineralogical Magazine  www.minersoc.org
Analysis of nanoscale Zero Valent Iron particles upon arrival at a monitoring well

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Nanoscale Zero Valent Iron (nZVI) has received significant attention in recent years due to its ability to rapidly destroy numerous priority source zone contaminants in controlled laboratory studies. This has led to great optimism surrounding nZVI particle injection for in situ remediation. However, rapid nanometal settling and poor mobility has been encountered, reportedly due to the ferromagnetic attractive forces between particles leading to agglomeration [1]. Studies have proposed different methods to screen attractive forces between nZVI particles [2, 3, 4], thus protecting them from agglomeration and preventing rapid settling. Although analytical techniques used to characterize particles confirm that these methods yield high quality particles that are stable and readily reactive for extended periods of time in the lab, several important questions remain.

How well can nZVI particles travel through the subsurface?
What is their state when they reach target contamination?
Do current methods used to detect nZVI particles in the lab lend themselves to field application?

In this field study existing synthesis techniques [2] were scaled up and 800L of nZVI was injected into a contaminated utility corridor containing various chlorinated solvents. nZVI particles intercepted by monitoring wells were analyzed using transmission electron microscopy and dynamic light scattering that characterize their size. The zero valent iron content of the particles was also compared to nZVI immediately after synthesis to gain insight into the characteristics of nZVI being delivered to the contamination.


Seismological constraints on an evolution of the Izu-Bonin intra-oceanic arc

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JAMSTEC has been conducting intensive active-source seismic surveys to cover the entire Izu-Bonin arc. New seismological constraints on formation and evolution processes of the arc crust are revealed from those data. For examples, a large volume of felsic-to-intermediate component crust having Vp of 6.0 - 6.8 km/s is predominantly observed beneath basaltic volcanic centers along the current volcanic front. We also discovered a similar along arc variation of the felsic-to-intermediate component crust in the rear-arc, which is proposed to be separated from the volcanic front after Oligocene. These findings suggest that the main part of the arc crust consisting of the felsic-to-intermediate component was created before the rear-arc has been separated from the volcanic front probably in Oligocene age. From recently obtained seismic data in the fore-arc, on the other hand, we found that the structure of the fore-arc region represents significantly different characters from that of the volcanic front. Petrological studies in the fore-arc region proposed a formation of oceanic crust associated with boninitic volcanism during an initial stage of subduction. The newly obtained seismic structures in the fore-arc strongly support this idea; i.e. the crust beneath the Bonin ridge in the fore-arc is remarkably thin (less than 10 km), and velocity-depth profiles in the fore-arc is almost identical to that of typical oceanic crust.

Magnesium isotope composition of presolar silicate grains

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We have measured the Mg isotope compositions of presolar silicate grains, to gain insights into the stellar nucleosynthesis and Galactic chemical evolution (GCE) of Mg isotopes.

More than half of the Mg in the interstellar medium (ISM) is hosted by oxide and silicate dust produced by evolved stars. The Mg isotopic composition of dust grains predate our Solar System could provide information about the Mg isotope inventory of the local ISM at the time of Solar System formation. This is of particular interest, as the $^{26}$Mg/$^{24}$Mg and $^{25}$Mg/$^{24}$Mg ratios of the Sun (and the Solar System) appear to be substantially lower than that predicted by GCE models for stars of solar metallicity ($Z_{\odot}$). Presolar silicate grains represent the silicate fraction of the interstellar dust at the time of Solar System formation. They are 200-300 nm crystalline or amorphous grains, which escaped Solar System processing, thereby retaining their pristine isotope compositions.

Presolar silicate grains of the present study were found in the matrix of Acre 094 (an ungrouped carbonaceous chondrite), based on their O isotope compositions and Si-Al-O systematics. These were determined by the NanoSIMS, as were the grains’ Mg isotope compositions (for analytical conditions see [5]). Based on their O isotope composition, the identified 26 grains were produced in the stellar winds of AGB stars, with initial masses (M) of 1.15-2.2 $M_{\odot}$, and Z $\sim Z_{\odot}$, similar to the majority (80%) of presolar silicates reported in the literature previously. Two of the 3 grains analysed for Mg isotopes so far have solar $^{25}$Mg/$^{24}$Mg ratios within analytical uncertainty (1σ) whereas a third grain shows a slight enrichment in $^{25}$Mg relative to solar ($\delta^{25}$Mg = 32 ± 20‰). The $^{25}$Mg-enriched grain also has elevated $^{26}$Mg/$^{24}$Mg ($\delta^{26}$Mg = 39 ± 20‰), as do one of the other two grains ($\delta^{26}$Mg = 56 ± 16‰). Interestingly, in a $\delta^{25}$Mg vs. $\delta^{26}$Mg plot our silicate grains fall along a line with slope $\sim 1$ as predicted by the GCE model of [2] for stars with $\sim$-solar Z; however, at much lower $^{25}$Mg/$^{24}$Mg and $^{26}$Mg/$^{24}$Mg ratios than predicted, similar to presolar oxide grains from akin stellar sources [7].

Fe acquisition from natural organic matter by an aerobic Pseudomonad: Siderophores and cellular Fe status

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Aerobic microorganisms have evolved various strategies to acquire nutrient Fe (often limiting in circumneutral environments), including the release of Fe-chelating siderophores. The potential importance of siderophores in Fe acquisition from natural organic matter (NOM) in the form of reverse osmosis (RO) and aquatic XAD-8-isolated humic samples (both with naturally associated Fe) was investigated using a wild type strain (WT) of aerobic Pseudomonas mendocina that produces siderophore (s) and an engineered mutant that cannot. Microbial growth under Fe-limited batch conditions was monitored via optical density, and a biosensor assay was used to report on transcriptional output as a measure of cellular Fe status. Both WT and mutant strains acquired Fe from NOM. Bacterially sensed Fe deficiency in the presence of the RO sample decreased with increasing [Fe] and was less for the WT than for the mutant. However, for both WT and mutant, maximum growth in the presence of the RO sample increased as: 1 mgC/L (0.2 µM Fe) < 100 mgC/L (20 µM Fe) < 1 mgC/L (2 µM Fe); the highest concentration of NOM appeared to diminish numbers of free-swimming/planktonic bacteria, perhaps by inducing biofilm formation and/or as a result of associated Al. Growth was slightly more robust on the XAD-8 compared to the RO sample at 2 µM Fe, although there were no apparent differences in internal Fe status. Chelex® treatment to partially remove metals associated with the RO sample increased Fe stress but did not substantially affect growth. It was concluded that: (1) siderophores are useful but not necessary for Fe acquisition from NOM by P. mendocina and (2) NOM may have complex effects on microbial growth, related not just to Fe content but potentially to the presence of other (trace)metals such as Al and/or to effects on biofilm development.

No differences in Sr isotope ratios between ectomycorrhizal and arbuscular mycorrhizal ecosystems across a wide range of geological substrates

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In highly weathered soils, where phosphorus (P) in particular may be a limiting nutrient, theory dictates that ectomycorrhizal (ECM) ecosystems are most efficient at uptake from mineral P through weathering of Ca-phosphate minerals and recycling of organic P. The ecological significance of mineral weathering by ECM fungi however remains unclear. We studied 10 pairs of pure arbuscular (AM) and pure ECM forests on different geological substrates on the South Island of New Zealand. Sr isotope ratios of dominant canopy tree foliage (AM *Dacrydium cupressinum* and ECM *Nothofagus menziesii*) were determined and in thin sections we analysed structural interactions between mycorrhizal hyphae and mineral and/or organic soil particles. Both AM and ECM forests had similar Sr isotope ratios that varied with geological substrates, indicating both forest types obtain Sr (and Ca-phosphate) from the same sources. Fungal weathering tunnels in feldspar grains were present in thin sections from both forest types. These preliminary data suggest there are no major differences in base cation nutrient uptake between AM and ECM ecosystems. This might challenge our understanding of the respective roles of ECM and AM fungi in ecosystem nutrient cycles.

Oceanic plagiogranites as products of hydrothermal activity at slow-spreading ridges

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We studied more than 100 oceanic gabbros from Mid-Atlantic Ridge and Southwest Indian Ridge by scanning electron microscopy and found in 90% of the samples microstructures suggesting that hydrous partial melting reactions proceeded. The best proxy for the underlying reaction is plagioclase strongly enriched in anorthite which is arranged in zones along grain boundaries implying that the partial melting process was triggered by fluids percolating on grain boundaries in a ductile regime. The composition of the new An-rich plagioclase is strongly impoverished in incompatible trace element excluding a model that these An-rich zones were precipitated by late, hydrous evolved melts. In some cases it is evidenced that the water-rich fluids are seawater-derived, suggesting a model that hydrothermal activity/circulation within the deep oceanic crust may trigger hydrous partial melting resulting in the production of oceanic plagiogranites, at temperatures exceeding 850° without any crack system, a prerequisite in current models for enabling hydrothermal circulation. This is in contrast with new findings of [1] stating that zircons of many plagiogranites from slow-spreading ridges show oxygen isotopes typically for equilibrium with mantle. However, new experimental work show that water activities prevailing during the melting reaction can be regarded as extremely low implying that a potential sea water source cannot be easily detected by stable isotopes.

Lithium-boron isotope fractionation during degassing of rhyolitic magma

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It has been considered that some volatile trace elements partition into a gas phase and leave the host magma during degassing events. For example, lithium and boron are light elements, which show strong affinity to fluid phase. Then, it is certainly possible to partition these elements into degassing fluid bubbles under pressure. Furthermore, during such element redistribution via diffusion transport, isotopes of lithium and boron may fractionate.

We have analyzed experimentally degassed natural rhyolitic obsidian, which was pre-saturated in H2O at 210 MPa, 800 °C giving approximately 6 wt%. These samples were isothermally decompressed at the rate of 1000 and 27.8 kPa/s. The final pressure before quench was approximately 70 MPa. Here, a rhyolitic composition was chosen for their ability to retain bubbles within the melt matrix. A maximum element exchange is expected between gas phase and melt, while element diffusivities are slower in rhyolite than basalt. The result shows that significant lithium and boron depletion in the host lava can take place within 12 min of isothermal decompression at 800 °C. The duration of bubble growth was 20 sec and 12 min depending on the decompression rate.

The fast and slow decompression resulted in heterogeneous lithium and boron abundance in the charge. The areas further away from bubbles have lithium and boron abundance indistinguishable from the starting glass, and the areas close to bubbles show 43 and 18 % depletion of lithium and boron, respectively, while H2O depletion is 50%. When significant abundance depletions were observed in the glass, in close vicinities, 7Li is enriched by as much as 20.2 ± 1.5 permil, and 11B is enriched by 8.8 ± 2.6 permil. The association of abundance depletion and heavy isotope enrichment strongly indicates isotope fractionation governed by diffusion transport.

Loparite composition in stratified Lovozero alkaline intrusion

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Lovozero massif, the largest of the Globe layered peralkaline intrusion, comprises super-large rare-metal (Nb, Ta, REE) deposit. The main ore mineral is loparite (Na, Ce, Ca)2 (Ti, Nb)2O6 which was mined during many years. Compositional evolution of loparite has been investigated through a 2.35 km section of the Lovozero massif using LA-ICP-MS Institut für Geowissenschaften, University Frankfurt and CAMECA SX50 British Museum of Natural History (London) (Kogarko et al. 2002). The composition of cumulus loparite changed systematically upward through the intrusion with an increase in Na, Sr, Nb, Th, Nb/Ta, U/Th and decrease in REE, Zr, V, Zn, Ba and Ti. Our investigation indicates that the formation of loparite ore was the result of several factors including the chemical evolution of high alkaline magmatic system and mechanical accumulation of loparite at the base of convecting unit.
Two- and three-dimensional imaging of platinum-group minerals at submicrometer scale with synchrotron X-ray

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Platinum-group elements (PGE) in the Earth’s mantle are key tracers for understanding the differentiation history of the Earth. PGE in mantle peridotite are strongly concentrated in Fe-Ni-Cu sulfides [1], whereas platinum-group minerals (PGM) are also potential phases that host significant amounts of PGE in the mantle [2, 3]. PGM are too small to be detected with conventional analytical methods, and therefore it is difficult to know how abundantly and where PGM exist in the mantle. PGM ever found in peridotite samples are mostly associated with Fe-Ni-Cu sulfides [3, 4], implying that those PGM had exsolved from the Fe-Ni-Cu sulfides [1]. On the other hand, discrete PGM grains have been found from a sulfide-free harzburgite [5], but these PGM are interpreted to be residues formed in response to the complete consumption of Fe-Ni-Cu sulfides during partial melting of peridotite. Textural and morphological investigation of PGM in peridotites at submicrometer scale could be a powerful method to know whether PGM found in peridotites had originally existed as discrete grains in the mantle.

We did two- and three-dimensional imaging of PGM in peridotite samples using synchrotron X-ray at SPring-8 to reveal morphology of PGM and their textural relationship with surrounding minerals. Three-dimensional mapping of PGM-bearing Fe-Ni-Cu sulfides with micro-XRF [4] demonstrated that PGM distributed near the rims of the sulfide grains. Three-dimensional imaging of them with X-ray computed tomography and laminography revealed that some PGM grains are included within the sulfide grain. These observation suggests that not all of the PGM are exsolution products from the Fe-Ni-Cu sulfides.

REFERENCES
Low-temperature thermochronology of the Mesozoic uplift history in the Hardangerfjord area, SW Norway

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The geology of the Hardangerfjord area is dominated by the Hardangerfjord Shear Zone (HSZ), a major crustal-scale structure that formed during Devonian extension shortly following the Caledonian orogeny. The HSZ might be part of an even larger zone of crustal deformation stretching across the North Sea into the Highland Boundary Fault in Scotland. The Hardangerfjord itself follows the trend of the shear zone and acted as one of the largest sediment pathways in the area. The amount of inland erosion and the corresponding depositional patterns are strongly affected by onshore tectonics.

The present project aims to constrain the amount and timing of post-Caledonian uplift in this area by fission track, (U-Th)/He and K/Ar dating. In particular the apparent absence of Mesozoic brittle reactivation of the HSZ in this area is targeted by sampling of detailed profiles parallel and across the HSZ. Furthermore, vertical profiles on steep flanks of the Hardangerfjord are analysed in order to obtain more precise uplift and erosion rates. This study will improve our understanding of onshore tectonic processes and their effect on offshore sedimentation cycles in the North Sea.

Subducted oceanic crust exhumed from the lower mantle

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Over the last 25 years diamonds from several continents have yielded inclusions that have been interpreted as sub-lithospheric in origin. The mineralogy and compositions of the inclusions have been interpreted in terms of both peridotitic and basaltic protoliths and a range of pressures. There is now an abundance of samples of basaltic inclusions that record transition zone and lower asthenospheric pressures [1], but until now there has been no convincing evidence for diamonds that crystallised in the lower mantle from a basaltic protolith.

In this study we report on a suite of mineral inclusions in diamonds from Juina, Brazil, which have exactly the mineralogy and chemistry expected for a basaltic composition at depths of 700-1200 km. Syngenetic, composite mineral inclusions in diamonds from a single kimberlite pipe (Juina 5) are found to have the bulk chemistries of the ‘calcium ferrite’ phase (CF-phase), ‘New Aluminium Silicate’ phase (NAL-phase), Al- and Fe-rich Mg-perovskite, and Ti-rich Ca perovskite. CF- and NAL-phases have previously been observed only in high pressure and temperature experiments on basaltic bulk compositions. The inclusions therefore indicate an origin of the diamonds and inclusions in oceanic crust subducted into the lower mantle.

The relatively high density of subducted basalt, especially if it is cooler than the surrounding peridotitic mantle, means that the mechanism for exhumation of basaltic crust from the lower mantle is puzzling. Available time constraints from other sub-lithospheric diamonds from the Juina region [2] indicate uplift rates of buoyant plumes of subducted material of ~ 1 – 50 cm/yr. Various subduction-exhumation cycles that can explain all the data will be discussed.

Mineralogical residence of Platinum Group Elements (PGE) in the Fe-Ni-Cu sulfide deposits of the Ivrea Verbano Zone (Italy)

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We present a residence-study of platinum group elements (PGE) in base metals sulfides (BMS) as well as in specific platinum group minerals (PGM). The PGE, Te and Re contents were analyzed by electron microprobe. The investigated Fe-Ni-Cu deposits of the Ivrea Verbano zone occur: 1) within layers of the igneous complex, 2) within an ultramafic sill intruding metasediments and 3) within ultramafic pipes intruding gabbros and metasediments.

PGE hosted by base metals sulfides (BMS)
Pyrrhotite (Po), pentlandite (Pn) and chalcopyrite (Ccp) were analyzed. Nearly two thirds of the analysis (n=349) contain Ir, Rh, Pt and Pd above detection limits (d.l.) (100, 32, 93 and 30 ppm). BMS from all the three types of deposits contain PGE. Generally Te is above d.l. (100 ppm); enriched in Pn. Different analyses of one specific mineral showed that the PGE are distributed dishomogeneously and that the quantities do not correlate with Te. Pt and Ir are mainly hosted by Po and Pn but not by Ccp. Pd is carried by each of the mentioned minerals. Rh occurs mainly in Po and only rare in Ccp and Pn. Re is only hosted by Po. Ir is enriched in Po and Pn and Ccp contains no Ir above d.l. Re was only detected in Po. Os data was neglect due to an interference with Cu. Ru was always below the d.l. of 35 ppm.

PGE hosted by platinum group minerals
We investigated several PGM included within the base metals sulfides (sizes <10 µm). The following species were found: Pd-rich melonite, merenskyite, moncheite, sperrylite and irarsite in decreasing order of abundance. According to the mineral chemistry, Te was partly substituted by Bi.

Our mineralogical observations suggest that the PGE, together with other chalcogens, were initially dissolved and collected by an immiscible sulfide liquid probably as small clusters. Subsequently, they were exsolved together with Te, Bi and As and crystallized as discrete PGM which are described for our investigated samples.

REE patterns in the ore-bearing of the Chortovo Koryto gold deposit (Eastern Siberia)

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REE are usually considered as inert components at the metamorphic and metasomatic processes. But in recent years more and more papers indicating their mobility in the hydrothermal systems are published. The REE distribution in the rock associations of the orogenic gold deposit Chortovo Koryto was studied by ICP-MS method.

This deposit is located on the boundary between Baikal-Patom fold-thrust belt and Siberian Craton. The gold ore are represented by system of quartz vein in the metamerrigenous slice of the Early Paleozoic formation Mikhailovskaya. The rock metamorphism corresponds to the greenschist facies. The composition of ore beds includes metaaleurolite - Qtz + Ab + Mus + Chl ± Bt (SiO₂: 60-80%; Al₂O₃: 8-19%; CaO: 0.1-0.6%; K₂O: 1.7-3.5%), carbonaceous slates - Qtz + Ab + Mus + Chl + C (SiO₂: 41-64%; Al₂O₃: 13-29%; CaO: 0.05-2.1%; K₂O: 1.9-6.8%), and altered rocks - Anc + Cal + Mus + Ab + Chl (SiO₂: 29-68%; Al₂O₃: 9-16%; CaO: 6-12%; K₂O: 1.4-7.6%).

The morphology of Chondrite normalized REE patterns of metaaleurolite is similar to the main sedimentary standards (La/Yb: 7.3-11.4; Eu/Eu*: 0.62-0.81), but differs in lower accumulation level of lanthanides (37-88 ppm). In the carbonaceous slates Σ REE increases up to 186 ppm mostly due to light REE (La/Yb: 18, 5-31, 2), at the same time an evident negative Eu anomaly is shown (Eu/Eu* 0.41-0.66). In the altered rocks a maximum enrichment (Σ TR: 251-875 ppm), lanthanides differentiation (La/Yb: 41, 3-50, 1) and absence of Eu anomaly (Eu/Eu* 0.89-1.02) are observed; from axil zone in direction of contacts Σ REE decreases from 413 to 251 ppm.

LILE and HFSE distribution in studied rocks indicates that the ore system was formed with presence of two source matters. Metaaleurolites and carbonaceous slates are compared with upper crust (Zr/Hf: 31.4-39.1; Ta/Nb: 12.02-17.01); altered rocks are similar to the rock basalt-andesite-rhyolite volcanic series of greenstone belts and they supplement with OIB.

The study was funded by Russian Ministry of Education and Science.
Phase relations of an Fe-Ni alloy determined in an internally-heated diamond anvil cell

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The Earth’s core is believed to contain several amounts of nickel while its major component is iron. In order to understand the nature of the Earth’s core, we conducted in situ X-ray diffraction study of an iron-nickel alloy in an internally-resistive heated diamond anvil cell (DAC) up to pressures (P) and temperatures (T) of 110 GPa and 2500 K. High-P-T experiments with the angle-dispersive X-ray diffraction system were conducted at the SPring-8. The improved internally heated DAC configuration provides stable heating with reliable temperature and pressure determination and phase identification [1]. Due to this configuration, we are able to put tight constraints on the P-T location and the width of the two phase loop of the \( \gamma \) (face-centered cubic structure) and \( \varepsilon \) (hexagonal close-packed structure) phase transition boundary. Results show that \( \gamma \) and \( \varepsilon \) transition boundary in Fe\( _{0.9}\)Ni\( _{0.1} \) is located at lower temperatures than that of pure iron, consistent with the previous works which used the laser-heated DAC [2, 3]. However, the width of the two-phase loop is narrower than those of previous works. We also evaluated the equation of state for the \( \varepsilon \) phase in Fe\( _{0.9}\)Ni\( _{0.1} \) from the compression data to P = 100 GPa.

We will present the P-T phase diagram and the density of \( \varepsilon \) phase in Fe\( _{0.9}\)Ni\( _{0.1} \), and discuss possible roles of the addition of nickel to iron in the Earth’s core.


Environmental geochemistry of Cu in agricultural soils treated with Cu-based fungicides

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Introduction
Copper-based fungicides (such as the Bordeaux mixture -\( \text{CuSO}_4 \cdot \text{Ca(OH)}_2 \), Cu-oxychloride etc.) have been extensively used in Europe since the end of the 19th century to control fungal diseases on vine, such as downy mildew caused by \( \text{Plasmopara viticola} \). Their long-term application and subsequent wash-off from the treated plants have resulted into extensive Cu accumulation in agricultural soils [1]. The aim of this paper is to provide information about the distribution, chemical fractionation and mobility of Cu in agricultural soils (vineyards, hop fields), including sorption processes and interactions with other commonly used organic fungicides (e.g. tebuconazole).

Results and Discussion
As in other contaminated soils, Cu in fungicide-impacted soils is mainly associated with the oxidizable and, to a lesser extent, with the reducible soil fraction, according to the soil organic matter and (hydr)oxide contents. The retention of Cu differs with the fungicide used (higher retention was observed for Cu originating from the Bordeaux mixture compared to Cu-oxychloride), which indicates that different retention processes occurs. The suggested mechanisms include: specific and non-specific adsorption (especially on soil organic matter) and precipitation of newly formed phases, such as CuO, Cu (OH)\(_2\), various Cu-hydroxysulfates etc. The retention of fungicide-derived Cu in the studied soil types can be well described by the Freundlich isotherm and is directly controlled by its chemical form [2]. The presence of other organic-based fungicides, e.g. tebuconazole, can alter the adsorption behavior of Cu due to speciation changes (e.g. formation of Cu-tebuconazole complexes) [3].

Observing the diurnal variability of Aerosol Optical Depth (AOD) from a geostationary satellite: Implications for air quality and climate monitoring

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NOAA has been providing AOD product from the GOES series of Imagers to users for a decade now. GOES AODs are derived from the single visible channel using a look-up-table approach; cloud screening is done using IR channels. GOES AODs, available at 30-minute temporal resolution and 4-km spatial resolution, have a root mean square error of 0.12; retrieval errors, however, are large when solar angles and/or view angles are large. Other sources of errors include cloud contamination, calibration errors, and errors in surface reflectance characterization. Analysis of GOES AODs over the United States indicates that spatial and temporal variability during pollution events is well captured; sub-urban/rural regions show good grid-to-grid correlation and the urban regions dominated by local pollution sources show less correlation with sub-urban regions. Analysis also shows that diurnal sampling improves the accuracy of monthly/seasonal mean AODs that has relevance to monitoring the impact of climate change. In addition to these results, we will show analysis of some case studies of pollution events that highlight the strengths of diurnal sampling with respect to policy implications as well as the capabilities of the future satellite instruments (e.g. GEO-CAPE) that will have better product accuracy and precision.

Gold-ore resources of Uzbekistan: Systematization and regularities of deposits’ location

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The principles of the classification of gold-ore deposits

While classifying a geology-industrial approach with emphasis on main minerals of ores (quartz, sercite, adularia, alunite, pyrite, arsenopyrite), high-, low-sulphidized types is used. It was found [1] that on all hydrothermal gold ore deposits of the world, independently from host environment, a standard row of mineral, correspondingly, geochemical types is shown: scheelite-molybdenite (Au-W), pyrite-arsenopyrite (Au-As), telluride-polymetallic (Au-Te), sulphosalt-silver (Au-Ag), antimonite-sulphoantimonite (Au-Sb), realgar-cinnabar (Au-Hg). A porphiritic (Au-Cu, Mo) type is marked separately. An industrial resource of the deposit is determined by 1-4 types.

Regularities of location and mineral-geochemical style

Uzbekistan is one of the leading countries in the world on reserves of gold. All deposits are located within the Kyzylkum-Kurama metallogenic belt and they form ore districts in the places of intersection of the Beltau-Kurama volcanoc-plutonic belt (BKVB) with deep faults. Each ore district is characterized by its mineral-geochemical style that is explained by different depth of the formation, hypogeo-, meso-, epithermal conditions. From the West to the East of the BKVB the role of later types from Au-W to Au-Sb-Hg types increases. Elements’ concentration coefficients in ores relatively to their clarks form following rows and mineral forms [2]: Muruntau – Bi-As-Te-Au-Se-Pd-W-Ag-Sb-Mo; tellurides of Bi, maldonite, arsenopyrite, scheelite, pyrite, pyrite, Co-Ni minerals. Charmitan – As-Te-Bi-Au-Sb-Se-As-Pb-Mo; Bi tellurides, maldonite, aurostibite, Pb-Ag-Se sulphoantimonites, arsenopyrite, pyrite. Kochbulak – Te-Au-Bi-Sb-Ag-Se-As-Cu-Pb-Sn; tellurides of Au, Ag, Bi, Sb, Pb, Cu, Hg; pyrite, goldfieldite, tetrahedrite. Kalmakyr – Te-Re-Bi-Mo-Au-Se-Cu-Ag-As-Sb; tellurides of Bi, Au, Ag; Re-molybdenite, chalcopyrite, pyrite.

According to the statistics [3] 5-6 medium size deposits (15-20 tonnes) and 25-28 small deposits (<15 tonnes) usually form around one big deposit (>100 tonnes). The resources of gold in Uzbekistan are highly evaluated.

Chromium enrichment in iron formations record Earth’s first acid rock drainage during the Great Oxidation Event

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Iron formations (IF) are iron rich (~20-40% Fe) and siliceous (~40-50% SiO₂) sedimentary deposits that precipitated throughout much of the Precambrian. Their trace element composition have been used as a proxy for ancient seawater chemistry, with the view of better understanding nutrient availability for the ancient marine biosphere [1, 2]. Recently, their composition have also provided new insights into the chemical weathering processes on land and the transfer of solutes to the ocean. For instance, a recent compilation of Cr enrichment in IF shows a profound enrichment at 2.48 Gyr, coincident with the advent of the Great Oxidation Event. Given the insolubility of Cr minerals, its mobilization and incorporation into IF indicates enhanced chemical weathering at that time, most likely associated with continental pyrite oxidation. Today, aerobic chemolithoautotrophic bacteria are essential to this process, catalysing the continued oxidation of Fe (II) as pH values drop below the threshold for inorganic Fe (II) oxidation. We suggest that the Cr pulse beginning 2.48 Gyr ago indicates that such bacteria began utilising O₂ for the first time to oxidise a previously stable and abundant crustal pyrite reservoir. Sulphuric acid generated by this metabolism ultimately leached Cr from ultramafic source rocks and residual soils. This profound shift in weathering regimes constitutes Earth’s first acid rock drainage and accounts for independent evidence for increased supply of sulphate and sulphide-hosted trace elements to the oceans at that time.


Deep versus shallow slab melt signatures recorded by Nb/Ta in modern island arc lavas

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The Solomon Islands cover over 1000 km of the SW Pacific plate border and constitute a modern intra-oceanic arc system devoid of subducted sediments and continental crust. Due to a change of subduction polarity, an Eocene deeply-subducted Pacific slab and a shallower, recently subducting Indian–Australian slab remain in the subarc mantle at depths of >100 km and 35-80 km, respectively [1]. Slab melt-related lavas from the Solomons therefore provide unique insights into the residual mineralogy of two slabs at different depths and their influence on the geochemical signatures of shallow and relatively deep slab melts.

Mafic to intermediate slab melt-related lavas from the southwestern volcanic chain of the Solomon Islands show the largest range of Nb/Ta ever reported in a single modern subduction environment. They range from low, subchondritic Nb/Ta (min. ~10) to superchondritic values (max. ~27) that correlate with slab melt signatures (e.g. Gd/Yb) [2]. Isotope dilution MC-ICP-MS data confirm this large range of Nb/Ta observed in Q-ICP-MS data. One minor slab melt component characterised by a low Nb/Ta is derived from the shallow and recently subducting Indian–Australian plate where amphibole is still a significant residual phase. In contrast, the high Nb/Ta signatures can only be explained by enrichment of the sub-arc mantle source by partial melts from subducted oceanic crust in the presence of residual rutile-bearing eclogite, where amphibole is either a minor phase or entirely absent. Only the old subducted Jurassic Pacific slab is located at depths required for such mineral assemblages. The slab melts that enriched the sub-arc mantle with an unusually high Nb/Ta signature are derived from an initially intact Pacific plate that was probably subject to a slab break-off event and subsequent melting at depths >100 km. Pb isotope data support a Pacific origin of these slab melts [3]. Altogether these geochemical constraints support recent geophysical studies in that partial slab melting may also affect initially intact oceanic plates older than 50 Ma [e.g. 4].

Groundwater depletion: A U.S. national assessment and global perspective

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Development of groundwater resources for agricultural, industrial, and municipal purposes greatly expanded during the 20th century, and economic gains from groundwater use have been dramatic. In many places, however, groundwater reserves have been depleted to the extent that well yields have decreased, pumping costs have increased, water quality has deteriorated, aquatic ecosystems have been damaged by reduced groundwater discharge, and land has subsided irreversibly. Some causes and effects of groundwater depletion are neither obvious nor easy to assess. If cumulative long-term global depletion is large, it will represent a substantial net transfer of mass from land to the oceans, thereby contributing to sea-level rise. Much groundwater pumped from confined aquifers is derived from storage losses in adjacent confining layers. Nevertheless, depletion in low-permeability layers is difficult to estimate, rarely monitored, and too often overlooked. A new simplified method for estimating depletion from confining layers was developed, tested, and applied. Results indicate that depletion in confining layers can greatly exceed the depletion from the confined aquifer itself. (For example, in the confined Dakota Aquifer, about 98 percent of the water removed from storage was derived from depletion in adjacent confining units.) A U.S. national groundwater depletion census indicates that about 800 km³ of water was depleted from groundwater systems in the U.S. during the 20th century—equivalent to a sea-level rise of approximately 2.2 mm. Long-term global groundwater depletion since 1900 totalled about 3,400 km³ through 2008, equivalent to a sea-level rise of approximately 9.3 and 12.6 mm, respectively. The rate of annual depletion has increased markedly since about 1950, with maximum rates occurring during the most recent period (2000-2008), when it averaged about 145 km³/yr (equivalent to 0.23 mm/yr of sea-level rise). This recent average rate would explain about 13 percent of the reported long-term rate of sea-level rise of 1.8 mm/yr. Worldwide, the magnitude of groundwater depletion is a small but nontrivial contribution to sea-level rise during the 20th century.

Discovery of new hydrothermal active fields in the South-West Pacific. Organic geochemistry of the fluids

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Back-arc basins in the South-West Pacific have been investigated for hydrothermal activity in the last 20 years. Several hydrothermal fields have been discovered in the Lau basin, Manus basin and North Fiji basin. A new area off-shore the Futuna island was surveyed in fall 2010 during a French cruise conducted by Ifremer and two new hydrothermal active fields (Amanaki and Kulo Lasi) were discovered. The plumes were first evidenced by the use of physical and geochemical tracers. At Kulo Lasi, nephelometry, Mn, CH₄, He profiles strongly correlated and consistently showed a maximal anomaly in the water column at about 1200 m depth. Concentrations of CH₄ up to 1200 nL.L⁻¹ and up to 30 nM for Mn were detected. High-resolution bathymetry supported the tracers indications, showing a caldeira in the vicinity culminating at 1200 m. Numerous small black smokers were then discovered on the seafloor during our first submersible dive. CTD profiles were recorded around and on the field during 9 CTD operations and 6 Nautile dives. Alongside, water column samples and hydrothermal fluids samples were collected. On the one hand, physics and geochemistry of the Kulo Lasi plume will be discussed here. On the other hand, relatively elevated concentrations of H₂ and CO₂ have been measured in the fluids from Kulo Lasi (gas and inorganic geochemistry of the fluids will be the focus of another presentation by J.L. Charlou). In the presence of H₂ and CO₂, catalytic abiotic reactions (e.g. Sabatier, Fischer Tropsch) may occur and generate hydrocarbons [1, 2]. Supercritical seawater (Pc = 298 bar, Tc = 407 °C) is a favourable media for cleavages, condensations, cyclisations, hydrolysis, oxidation, hydrogenation and hydroformylation. A great variety of organic compounds (heavier hydrocarbons, prebiotic molecules [3, 4]) may thus be produced at the Kulo Lasi hydrothermal field. The preliminary results on the organic geochemistry of the hot fluids will be presented here.

**Thermodynamic and trace element modeling to quantify fluid fluxes and fluid-rock interaction in high pressure rocks from the Sesia Zone (Western Alps)**

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The amount and composition of fluids percolating through high pressure rocks and the effect of resulting fluid-rock interaction on fluid and wall rock composition has been constrained by thermodynamic and trace element modeling of partially overprinted blueschist-facies rocks from the Sesia Zone (Western Alps). Deformation-induced differences in fluid flux led to a partial preservation of pristine mineral cores in weakly deformed phengite and sodic amphibole grains that were used to quantify Li, B, Sr and Pb distribution during mineral growth, breakdown and modification induced by fluid-rock interaction. Our results show that Li and B budgets are strongly fluid-controlled, thus acting as excellent tracers for fluid-rock interaction processes, whereas Sr and Pb budgets in our samples are mainly controlled by the fluid-induced formation of epidote. Our calculations show that fluid-rock interaction caused significant Li and B depletion in the affected rocks due to leaching effects, which in turn leads to an up to five-fold enrichment of these elements in the percolating fluid. Depending on available fluid-mineral trace element distribution coefficients modeled fluid rock ratios necessary to produce the observed trace element patterns in the affected minerals were up to 1 in weakly deformed samples and at least 1 – 4 in shear zone mylonites. These values can be used to determine time integrated fluid fluxes that were up to 4. $10^3$ m$^3$-m$^{-2}$ in the weakly deformed rocks and at least 2 – 8. $10^3$ m$^3$-m$^{-2}$ in the mylonites. Combined thermodynamic and trace element models help to quantify metamorphic fluid fluxes and the associated element transfer in complex, reacting rock systems and to better understand commonly observed fluid-induced trace element trends in metamorphic and magmatic rocks and minerals from different geodynamic environments.

**Evidence for a Hawaii-Emperor bend in the Rurutu hotspot track**

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Hotspots have long been used as an absolute and fixed reference frame for modeling plate motions. However, the paths of hotspot tracks may be complicated by factors related to mantle flow and/or plume motion. The two longest, continuous hotspot tracks recognized on the Pacific Plate, the Hawaiian-Emperor and Louisville chains, exhibit different behavior prior to ~50 Ma, where the Hawaiian-Emperor chain shows a pronounced ‘kink’, while the Louisville chain is gently curved [1]. Furthermore, the Hawaiian hotspot might have incurred a ~15° southern shift between 80 and 50 Ma, while the Louisville hotspot seems to have behaved more stationary (or moving west to east) over the same time period. The causes of these differences are not well understood, and they have some important ramifications for absolute plate motion models and our understanding of mantle dynamics. Despite suggestions to retire the plume hypothesis, a more conciliatory view explains the variety of observations with three different types of hotspots. This would imply the major hotspots may still reflect plate motion with respect to the mantle, although a component of plume motion could also be recorded by the orientation of a volcanic chain.

Recent geochemical evidence and radiometric ages suggest that the Rurutu hotspot is long-lived (100 Ma) [2, 3] and follows a track midway between Hawaii and Louisville. Like Hawaii, the Rurutu hotspot exhibits a sharp bend in the Tuvalu region between Samoa and the Gilberts Ridge, around 35-55 Ma following the latest absolute plate motion models. The hotspot volcanoes are characterized by HIMU-type isotopic compositions [3], distinguishing them from other hotspots such as Samoa [4]. Therefore, the Rurutu hotspot may provide a third, long-lived Pacific hotspot track that can help to deconvolve the effects of plate motion from plume motion in determining the paths of hotspot tracks.

Trace element systematics in HT metamorphic rutile: The robustness of the Zr geothermometer

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The Zr-in-rutile thermometer [1] has been successfully applied to a wide range of high-grade metamorphic rocks. However, experimental data indicate that rutile may be only moderately retentive to Zr [2]. Some field-based studies reported a large range of Zr concentrations from granulite facies metamorphic rocks suggesting post-peak diffusional resetting during slow cooling [3]. Further investigation into the Zr systematics in rutile is needed to improve the interpretation of Zr-in-rutile temperature estimates.

For this purpose, we analyzed rutile grains from zircon-bearing granulite-facies metapelites of the Archaean Pikwitonei granulite domain, Canada. The Zr concentrations were evaluated by acquiring compositional profiles and maps by electron probe micro-analysis. Profiles of Nb, Cr and V, which diffuse faster in rutile than Zr [4], were analyzed simultaneously. The variation in the concentrations of all elements is small within individual rutile grains (120-280 μm) from 3 different samples, but large differences are observed between grains only millimeters apart in the same sample.

The lack of diffusion profiles for all analyzed elements indicates that Zr concentrations are pristine. Zoning of high-Zr rutile (3000-4600 ppm) demonstrates Zr undersaturation during growth under dry UHT conditions in spite of the presence of zircon. Therefore, several rutile grains should be analyzed in a sample to obtain a useful minimum peak temperature estimate. The highest Zr-in-rutile temperatures for the samples from the Pikwitonei granulite domain are ca. 900 °C and thus exceed previous estimates of 820 °C based on two-feldspar thermometry [5], demonstrating the advantage of Zr-in-rutile thermometry for constraining peak temperatures of UHT rocks.


In situ analysis of U-Th disequilibria in titanite by fs-LA-MC-ICPMS

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A new technique for in situ analysis of U-Th disequilibria in titanite by fs-LA-MC-ICPMS is presented. An in-house titanite glass ([U] = 215 ppm), determined to be in secular equilibrium by solution mode MC-ICPMS, is used to correct for U-Th elemental fractionation by sample standard bracketing. SEM-Faraday gain and abundance sensitivity are determined on solution standards interspersed every 15 laser ablation analysis.

The effect of instrument settings to the accuracy and precision of (230Th/238U) ratios was investigated by multiple analyses of secondary titanite standards. The laser analysis mode (scanning or spot), laser energy and wavelength, and titanite material properties were all found to variably influence the U-Th elemental fractionation and compromise the accuracy of the data to different extents.

During spot analyses using near infra-red (NIR) wavelength and high laser energy, time-dependent elemental fractionation is observed, resulting in relatively large standard errors on the (230Th/238U). Decreasing the laser energy significantly reduces the time-dependent elemental fractionation but does not eliminate it completely, e.g. 2RSE on (230Th/238U) are 5.2% instead of 19%. NIR scanning mode analyses are not compromised by time-dependent elemental fractionation compared to solution mode analyses of secondary titanite standards. The effect of adjusting plasma conditions, with the aim to reduce the elemental fractionation, is currently investigated.
Preliminary results from Integrated Ocean Drilling Program Expedition 330 to the Louisville Seamount Trail

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Integrated Ocean Drilling Program (IODP) Expedition 330 drilled five different guyots in the Louisville Seamount Trail ranging in age between 80 and 50 Ma. The primary goals of this expedition were to drill a sufficiently large number of in situ lava flows at each seamount for high-quality estimates of their paleolatitudes using paleomagnetic measurements, for improving the overall age progression using high-precision 40Ar/39Ar geochronology, and for detailed geochemical studies of the volcanic evolution of these seamounts. With these data we can provide the unique record of the paleolatitude shift (or lack thereof) of the Louisville mantle plume and compare it with the ~15° paleolatitude shift observed for seamounts in the Hawaiian-Emperor Seamount Trail over the same time period. It also allows us to directly compare the geochemical evolution of a typical Louisville seamount with seamounts in Hawaii and to test the apparent long-lived homogeneous geochemical character of the Louisville mantle source. These comparisons are of fundamental importance to determine whether these two primary hotspots have moved coherently or not, and to understand the nature of hotspots and convection in the Earth's mantle. Finally, the paleolatitude, age and geochemical data together will provide a more advanced test of whether the Louisville seamounts were formed from the same mantle source that also formed the Ontong Java Plateau. If this is found to be the case, it is possible that the plume head of the Louisville mantle upwelling caused the massive LIP volcanism that formed the Ontong Java Plateau around 120 Ma and at an average 24±2°S paleolatitude.

Diamondiferous conglomerate preserves evidence for kimberlite and the deep cratonic root of the Mesoarchean Southern Superior craton

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Current models of the Superior craton growth invoke formation of the cold diamondiferous root soon after the 2.7 Ga orogeny that consolidated the craton. We show that the Superior craton included an older cratonic nucleus that had developed the deep diamondiferous root prior to 2.7 Ga, and also provide evidence for a Mesoarchean Superoir kimberlite. This evidence contradicts current views that Archean diamondiferous volcanics differed from kimberlites, which became a major diamond–bearing primary rock only in the Proterozoic.

The evidence is found in 2.697-2.701 Ga diamondiferous conglomerates of the Michipicoten Greenstone Belt (MGB) of the Wawa subprovince. The conglomerate metamorphosed in the greenschist facies contains mainly lithic igneous mafic to felsic clasts of local provenance. The conglomerate matrix includes diamonds and paragenetic diamond indicator minerals with subtle signs of mechanical abrasion and varying degrees of chemical resorption. The diamonds are predominantly white single octahedral crystals. Comparison of the size distribution, resorption and N aggregation of diamonds in Wawa lamprophyres and the conglomerate diamonds confirms that the latter did not derive from the proximal lamprophyric source. Heavy minerals panned from the conglomerate and extracted in commercial labs include Cr-diopside, olivine, corundum, chromite, anorthite, magnetite, pyrope with kelyphitic rims and picroilmenite. Low abundances of heavy minerals (several grains per 4-70 tonnes of the conglomerate) are, in part, explained by their complete or partial replacement by the greenschist assemblage. Cr-diopside, olivine, chromite and anorthite were derived from mafic-ultramafic anorhostes- and chromitite-bearing layered complexes mapped in the MGB. Corundum may have come from kimberlites or other mafic rocks as the majority of corundum is the Cr-bearing ruby. The presence of pyrope with more than 6 wt% Cr2O3 suggests derivation from the cratonic root, as such high-Cr pyrope are never found in the off cratonic continental or oceanic mantle. Picroilmenite has compositions typical of kimberlite and unlike that of ultramafic lamprophyres and other volcanics transitional to kimberlites. The Wawa conglomerate, therefore, should be considered analogous to the Witwatersrand conglomerate in recording indirect evidence for the Mesoarchean kimberlites.
Monitoring of plagiogranite of the Yeşilova Ophiolite: Geochemistry and confocal Raman spectroscopy, Southwest Anatolia, Turkey

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In most ophiolitic suites observed around the world, there are small bodies of intrusive leucocratic rocks, usually called plagiogranites. It has clear differences from other subunits of the ophiolite in colour, texture and geochemical character. Yeşilova ophiolite exhibits an incomplete oceanic crust stratigraphy with missing sheeted dykes and epicoceanic sediments. It is composed of tectonites, ultramafic-mafic cumulates, iso trope gabbros, plagiogranites and pillow basalts from the bottom to the top. Diabase and microgabbro usually cross-cut the peridotites. Plagiogranites crop out as veins, from the bottom to the top. Diabase and microgabbro usually cumulates, isotrope gabbros, plagiogranites and pillow basalts characterized by high SiO₂ (73.44±2.81) with remarkably low groundmass texture under the microscope.

Mainly characterized by the micrographic and myrmekitic plagiogranites have hypidiomorphic granular texture and supported by the Confocal Raman spectrometry. Of quartz, plagioclase, uralitized pyroxene, opaque minerals, color and fine to medium-grain size, consisting predominantly gabbro having a sharp contact. They have light green, white in dikes and small intrusive bodies intruded into the isotrope gabbro having a sharp contact. They have light green, white in color and fine to medium-grain size, consisting predominantly of quartz, plagioclase, uralitized pyroxene, opaque minerals and supported by the Confocal Raman spectrometry. Plagiogranites have hypidiomorphic granular texture and mainly characterized by the micrographic and myrmekitic groundmass texture under the microscope.

Whole-rock geochemical of plagiogranites are characterized by high SiO₂ (73.44±2.81) with remarkably low K₂O (0.62±0.48), and generally higher MgO (1.66±1.30), CaO (3.89±1.82) than the continental granite. Moreover; they have slightly high amount of Fe₂O₃/MgO ratio and similar Rb, Sr and Zr values to oceanic plagiogranite composition. On variation diagrams, CaO, Fe₂O₃, Sr, V, Co and Ta display clear negative correlations, whereas Na₂O, P₂O₅, Y, Zr, Hf, La, Ce show positive correlation with increasing of SiO₂ ratio. These can be explained by fraction crystallization processes in the late stage of magma generation. Plagiogranite samples display enrichment in LILE relative to HFSE in MORB and ORG normalized multi-element diagrams. In these diagrams, they exhibit depletions in Rb, Ba, Nb, P and Ti as characteristics of subduction-related magmas. Rare earth element (REE) patterns for plagiogranite show REE enrichment with respect to chondrite values. They exhibit slightly depletion in LREE ((La/Sm)N = 1.43-2.83) relative to HREE ((Sm/Lu)N = 0.43-0.92). Furthermore, all the samples of the plagiogranites have small positive Eu anomalies ((Eu/Eu*)N = 1.14-1.35), indicating the significant role of plagioclase in the fractional crystallization.

As a result, despite the lack of isotopic data, the petrographic and geochemical results suggest that plagiogranites of the Yeşilova ophiolite are the most probably related to crystal-liquid differentiation process of the oceanic crust of the Alpine belt.

Urban dead seas: Natural and anthropogenic influences on redox-stratified lakes and wetlands

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Redox-stratification is a pervasive feature of dynamic near-surface earth systems, occurring on scales of micrometers to kilometers. Examples can be found in systems as diverse as microbial mats, soils and sediment pore waters, groundwaters, lakes and seas. Physical processes, such as advective flow through pores or wind mixing of surface waters, interact with chemical factors, for instance the availability of electron acceptors and donors, and biological processes, including organic matter fixation, macrophyte root exudation, bioirrigation, bioturbation and microbially-mediated reactions, to produce spatially and temporally heterogeneous systems.

Anthropogenic activities can also have an enormous influence on redox-stratified systems. For example, the addition of limiting nutrients and labile organic matter to surface and groundwaters leads to substantial, widespread problems such as eutrophication and the creation of dead zones. There is increasing recognition that the introduction of other contaminants, such as road salt deicers, may also have important biogeochemical consequences, albeit often through subtle or indirect effects. Deciers, typically NaCl or CaCl₂, are applied in enormous and growing quantities in urbanized settings throughout the world. In the U.S. alone, >15,000,000 tons of decier are applied to roads each year. It is well-known that application of these salts can have a profound impact on macro- and micro- biological communities, yet remarkably few studies have examined the effects on biogeochemical processes.

Recent work suggests that such effects could be quite significant. For example, mesocosm data show that addition of NaCl, and especially CaCl₂, can stimulate anaerobic respiration in wetland soils. Furthermore, an increasing body of literature demonstrates that road salt deicers may suppress physical mixing in lakes, potentially resulting in transition from dimictic to monomictic or even meromictic conditions, and in pronounced redox-stratification of lake column waters. Particularly in eutrophic urban lakes, this is expected to have enormous consequences for biogeochemical cycling, and could lead to saline, persistently anoxic lake bottomwaters: ‘urban dead seas’. This emerging environmental problem deserves greater attention and further study.
Cr(VI) adsorption on γ-alumina
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Cr (VI) is a toxic contaminant that has been introduced into numerous surface and subsurface systems through industrial activities such as electroplating, leather tanning and steel manufacturing. In solution, it forms anionic complexes (CrO₄²⁻, HCrO₄⁻), and as such, may bind to the surfaces of positively charged solids. High surface area, synthetic γ-alumina is often used as an analog for aluminum oxides found in soils and sediments. It has a high point of zero charge (~5.5-8.9), and thus may bind Cr (VI) even at relatively high pH. However, few studies have investigated Cr (VI) sorption on γ-alumina.

In this study, Cr (VI) sorption on γ-alumina (N₂ BET SA = 233 m²/g) was measured as a function of pH (3-10), ionic strength (0.1 to 0.001 M NaNO₃), and pCO₂ (0, atmospheric, 2.5%). A large batch slurry of 2 g/L γ-alumina with 10⁻⁵ or 10⁻⁶ M Cr (VI) was titrated from pH 3 to 10, with aliquots removed at ~0.5 pH intervals. Individual aliquots were further equilibrated for 4 hrs, after which the supernatant was removed by centrifugation and syringe-filtration and analyzed for Cr (VI) by UV-vis spectrophotometry (diphenylcarbazide method) or for total Cr by ICP-OES using matrix-matched calibration standards.

Cr (VI) sorption is rapid, reaching equilibrium within 15 minutes, and is reversible, with 100% desorption occurring within 24 hrs. As expected, sorption decreases with increasing pH. For a given solution condition, more Cr (VI) uptake occurs in the 10⁻⁶ M compared to the 10⁻⁵ M Cr (VI) experiments. Adsorption edges show little dependence on ionic strength or pCO₂, except that Cr (VI) sorption is suppressed at low pH in experiments with high ionic strength and high pCO₂.

The measured adsorption edges were individually modeled using constant capacitance, diffuse double layer and triple layer surface complexation models. For each model, multiple site density, protonation/deprotonation stability constants, Cr (VI) reaction stoichiometries and capacitances were tested. In each case, good fits could be produced for individual edges. However, none of the models tested resulted in satisfactory fits over the complete range of measured pH, ionic strength, sorbate/sorbent, and pCO₂ conditions. The best fits were obtained using a constant capacitance model, because stability constants for this model are ionic-strength dependent.

Timing of denudation, erosion and surface uplift of the Hunza Karakoram – A case study of combined thermochronological and geomorphological approaches
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Geomorphological records of extreme surface uplifts of the Hunza Karakoram in the late Cenozoic are correlated with thermochronological history of relevant crystalline rocks during active collision orogeny. A set of studied samples dated by apatite fission-track (AFT) technique come from the SW-NE transect in the Hispar and Gharesa regions of the Hunza Karakoram. Variable lithological types of crystalline rocks were collected from 2 400 to 5 600 m a. s. l. and yielded ages between 3.9 ± 0.2 Ma to 9.7 ± 0.4 Ma. Our results confirmed effective denudation, erosion and transport of near-surface rock masses during the late Cenozoic.

Time-temperature modeling of AFT samples from the Hunza Karakoram shows a similar thermal history style, involving a period of total thermal annealing and a subsequent period of cooling corresponding to considerable denudation and erosion processes. Two dominant trends of cooling rate have been observed: (1) the Upper-Miocene to Pliocene period of a slow rate about 0.1 km/Ma followed by (2) the Quaternary period of a relatively rapid rate about 2.6 km/Ma. The later period of cooling can be associated with an approaching of (sampled) rock assemblages nearby late Cenozoic denudation and/or erosion surfaces.

Measured track-lengths vary from 10.3 ± 2.8 µm to 12.1 ± 2.2 µm with a negative skewness. The track-lengths-frequency histogram demonstrate a bimodal distribution with a short peak representing the higher temperature tracks and also with longer peaks derived from final cooling. These data give evidence of mixed ages as a result of (at least) two-stage cooling history of studied crystalline rocks.

Denudation and erosion of rock masses in the Hunza Karakoram estimated by a combination of current elevations of samples and depths of fossil apatite partial annealing zones reached up to 4 km from the Upper Miocene to the present.
Modern natural and technogenic iodine biogeochemical provinces: Spatial structure and health effects

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The ubiquity of living matter proved its chemical coevolution with and adaptation to the Earth geochemical environment. However the existence of homeostatic concentration intervals providing normal functioning of biosystems has led to formation of endemic species and/or distribution of regional and local biogeochemical endemic diseases in cases of expansion of species to environments with concentrations outside thresholds or catastrophic releases of chemical elements and/or compounds. A failure of regulatory mechanisms in at least 20% of population may be a criterion for biogeochemical province with endemy [1].

The main goal of our study was to reveal and analyze the structures of natural and technogenic geofields of iodine in soil and food chain components and iodine-dependent medical effects.

The study of Bryansk oblast affected by the Cherobyl fallout included: 1) estimation of the initial radioiodine contamination; 2) cartographic estimation of the soil iodine status; 3) determination of iodine in drinking water, milk, pasture plants, arable soil in private farms of 100 rural settlements provided with medical data on renal iodine excretion, endemic goiter and thyroid cancer.

Analysis of the obtained data organized as GIS data base allowed performing spatially adequate comparison of the geochemical and medical data and contouring of potential risk zones as a superposition of geofields of iodine.

The work has been supported by Russian foundation of basic research (grants #07-10-00912 [2] and 10-05-01148).


Raman spectroscopy of sodium silicates and germanates

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The approach to melt description we use here bases on idea of structural units make the basis of crystal chemistry of silicates and, when connected with one another via bridging bonds, form composite anions in melts or a disordered network in glass. The germanate system is of interest because of their analogy to silicates at high-pressure conditions. The local structure of silicate system can be presented as a set of silicon-oxygen tetrahedrons with various proportions of bridging and non-bridging oxygen atoms (Qn-units, where n is the number of bridging oxygen atoms). The coordination number of germanium atoms in glasses has attracted much attention due to a network forming cation can be in 4-coordinated and 6-coordinated states.

The concentrations of structural units Qn can be determined experimentally by techniques of Raman spectroscopy, which has no principal limitations in terms of temperature, so that in situ structural studies can be carried on in melts. Sodium silicates and germanates of x%Na2O·(100-x)%MO2 composition, where M = Si or Ge, x = 33, 40, 50, 55 ± 60 were synthesized from sodium carbonate and SiO2 (GeO2). To study the quantity dependence of structural units presented in glass (melt) from modifier content and temperature spectra were deconvoluted on Gaussian components.

The work was supported by the Russian Foundation for Basic Research (grant № 10-05-96044) and grant of President of Russian Federation (MK-109.2011.5).
Early and Middle Jurassic $\delta^{13}$C and $\delta^{18}$O trends: A high resolution dataset from the UK

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Low-Mg-calcite fossils have been extensively utilized to obtain past seawater chemistry and to reveal major environmental changes in Earth history [1, 2]. The resolution of these first generation long-term studies is often at biziozoic levels only. Recent work on major Phanerozoic events showed that distinctly higher resolutions are possible, revealing short-term stable isotope fluctuations and helping to discover its causes. Here we present new carbon and oxygen isotope data from mollusks and brachiopods collected from marine Early to Middle Jurassic successions of the UK representing a new generation of data in terms of temporal resolution. Together with literature data for the T–J boundary [3] and the Toarcian OAE [4] a nearly complete high-resolution record is now available. The fossils have been screened by various techniques, such as scanning electron microscopy and chemical analysis, to check for post-depositional alteration. The carbon isotope fluctuations obtained from the analyzed samples are the following: (1) a positive excursion in the earliest Sinemurian Conybeari zone, (2) a negative shift in the Sinemurian Bucklandi zone, (3) a negative excursion at the Sinemurian–Pliensbachian boundary (upper varicostatum and lower jamesoni zones), and (4) a positive excursion in the Late Pliensbachian margaritatus zone. The new oxygen isotope fluctuations in general correspond to those of the carbon isotopes, but with the exception for the Sinemurian–Pliensbachian boundary event, which is characterized by a positive $\delta^{18}$O trend during the negative $\delta^{13}$C excursion. This positive trend represents most likely bottom water cooling as a result of the Early Pliensbachian transgression. In addition, an Aalenian–Bajocian positive $\delta^{18}$O excursion is identified. The new high resolution dataset shows partly a strong similarity between the positions of the global warming and cooling events within transgressive and regressive phases of second-order depositional sequences though the Early Jurassic supporting the idea that second-order depositional sequences are a result of eustatic sea-level changes at that time.


Geo-bio interactions in hydrothermal fluids and their potential role for hydrothermal metal fluxes

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Hydrothermal vents emit fluids with high concentrations of many metals at the seafloor. Until recently it was assumed that the precipitation of most metals (e.g. Cu and Fe) during mixing with seawater reduces their net fluxes from the hydrothermal systems into the open ocean to negligible values. However, the recent discovery of significant organic complexation of Cu and Fe in the hydrothermal fluids and rising plumes, has urged a revision of trace metal fluxes from deep-sea hydrothermal vents. We demonstrated using field data and geochemical modeling [1] that the presence of organic ligands stabilizing dissolved trace metals strongly competes with metal precipitation and significantly increases the dissolved metal concentrations in hydrothermal fluids and plumes. According to our calculations, hydrothermal metal fluxes may be significantly larger than previously assumed, i.e. up to 20% of the deep-ocean dissolved Fe and Cu budget can be assigned to hydrothermal sources.

While the importance of organic ligands for hydrothermal metal fluxes seems to be acknowledged by now, the nature and origin of these organic molecules is still unclear. Amino acids, probably of biogenic origin, which have been found in significant concentrations in hydrothermal fluids [2], and other organic molecules containing thiol groups were potential candidates for stable metal complexation. In lab experiments with hydrothermal microbial cultures along Cu concentration gradients the production of organic Cu-binding ligands by the microbial communities due to increasing Cu stress was studied. Ligand production increased significantly with increasing Cu concentrations, implying microbial influence on dissolved metal concentrations, speciation and mineral precipitation in the hydrothermal vent environment. Our work suggests a significant modification of hydrothermal fluid chemistry and hydrothermal metal fluxes by biological processes.

Fluid inclusion study of a sediment-hosted copper ore deposit in the Lubin area (Poland)

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The sediment-hosted copper ore deposit in the Fore-Sudetic Monocline (Lubin area, SW Poland) is one of the largest in the world. Copper mineralization (Cu and Cu-Fe sulphides) follows a redox front (Rote Fäule) and occurs close to the contact between the uppermost Lower Permian terrestrial sandstones (Rotliegendes), and Upper Permian (Zechstein) marine deposits (including siliciclastics, shales, dolomites, and evaporates). Mineralization is characteristically vertically zoned, and the sulphide type is unrelated to the host-rock lithology. This deposit is believed to be an equivalent to the German Kupferschiefer copper ore formation.

Processes leading to the ore formation in the Lubin region can be better understood with a modern fluid inclusion study, combining of classical microthermometry with LA-ICP-MS analysis. This provides valuable data on temperature, pressure and chemical composition (including concentrations of major and trace elements in individual fluid inclusions) of the hydrothermal fluids.

Samples collected from the three deep mines (Lubin, Rudna and Polkowice-Sieroszowic) represent a variety of rock types (from both oxidized and reduced zones). Fluid inclusions were found in various rock types, but the most abundant are calcite veins and calcite infills of cavities in dolomites. Fluid inclusions are generally very small (<10µm), but diameters range up to 20-50 µm. Three main fluid inclusion types were identified: (1) aqueous two-phase primary fluid inclusions of irregular shapes, with small vapor bubble sizes (5-10 vol.%); (2) square single-phase aqueous fluid inclusions, distributed in the outer parts of the crystals; and, (3) very small secondary aqueous fluid inclusions with medium vapor bubble sizes (30 vol.%), present in late cracks.

Our combined microthermometry and LA-ICP-MS analysis provides the first data on the origin and geochemical evolution of low-temperature hydrothermal fluids in the Polish Kupferschiefer ore formation.

Extreme pressure dependence of sulphur solubility in silicate melts (experimental data)

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Physicochemical conditions of sulphur concentration within fluid-bearing magmas in the upper mantle and the earth crust during sulphide-silicate immiscibility are very important for understanding of origin of magmatic sulphide deposits. Influence of pressure on solubility of sulphur is still controversial [1-3].

We studied influence of pressure on the SCSS (sulphur concentration at sulphide saturation) in H2O and H2O+CO2-bearing silicate melts. We used Pt-peridotite ampoules filled with powder of olivine basalt and synthetic sulphide Fe30Ni30Cu30S10 as starting compositions. The highest concentrations of sulphur were 0.88-1.01 and 0.2 wt.% in H2O-and H2O+CO2-bearing silicate melts respectively at 1.5-2.0 GPa (Fig. 1). The minimum concentrations were 0.1-0.2 wt.% both at low (0.1-0.8 GPa) and high (2.5-4.0 GPa) pressure.

Figure 1: Relationships between pressure and SCSS in H2O- and H2O+CO2-bearing silicate melts.

Inversion of relationships between pressure and SCSS in H2O- and H2O+CO2-bearing silicate melts at P=1.5-2.0 GPa can be related to the inversion of volume effect of reactions and speciation of C, O, H and S in basalt melts at different pressure. Such inversion can play an important role in transport of sulphide sulphur and ore elements from the deep magmatic centres to the upper levels of the Earth crust where most of known sulphide ore deposits were discovered.

New geochronological U–Pb isotopic
data of granitoids from the Kuznetsk
Alatau Ridge, SW Siberia
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The Kuznetsk Alatau is a part of the Central-Asian mobile
belt (CAMB) and represents the ensemble of the Caledonian
fold-thrust structures. The Early Paleozoic large granitoid
intrusives are extensively distributed on its south-east slope.
The recent U-Pb isotope-geochronological data (SHRIMP-II)
obtained by us from sparse grains of the accessory zircon
enable three time borders to be established for the
manifestation of the granitoid magmatism.

We have studied two massifs of the derivatives of the
earliest Martaiga complex of the Middle Cambrian which are
composed by quartz diorites, tonalites, granodiorites and
plagiogranites. By the quartz diorites from these massifs, the
concordant age of their intrusion has been established
subsequently, at the Cambrian-Ordovician transition, the
formation of the Tigertysh granite complex has been in
progress. The dating of granitoids in its three satellites has
demonstrated the similar concordant age of their formation –
\( T = 510 \pm 7 \) and \( 506 \pm 4 \)
Ma. In the closing stage of the development of the Early Paleozoic granitoid magmatism, the
numerous small intrusions of the mixed composition has been
going on in the region: from quartz-monzonites and diorite-
porphyrites to granites and granite-porphyries. The isotopic
dates \( T = 432 \pm 4; 431 \pm 6; 429 \pm 6; 425 \pm 4 \)
Ma have been obtained from four rock varieties. This suggests the
comparatively narrow time interval (Llandovery – Wenlock)
for the final magmatic events in the Early Paleozoic. We
assume that granitoids from the SE slope of the Kuznetsk
Alatau aged 510–493 Ma, along with ultrabasite-basite
massifs, granite batholites, alkali basaltoids, complexes of
alkali rocks and carbonatites of the Caledonian stage of
development CAMB (~ 510–470 Ma) seem to form the Early
Paleozoic Large Igneous Province in its limits [1–3].

This study was funded by the Ministry of Education and
Science of Russian Federation (project 2.1.1/208, Federal
program of ‘Scientific and Scientific-Educational Personnel of
Innovative Russia 2009-2013).

Discovery of diamond and coesite in Bohemian granulites

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Microdiamond and coesite have been discovered in high-pressure granulites of North Bohemia. The newly found, 5-30 μm sized microdiamonds, documented by micro-Raman, occur as inclusions in garnet, kyanite and zircon. They range from well-formed octahedra in kyanite to ragged sub-rounded crystals in places forming clusters in garnet. Within garnet microdiamond commonly occurs with graphite, which forms also diamond-free aggregates of up to 0.1 mm in diameter with associated phases apatite, rutile, quartz and carbonate minerals whereas in kyanite associated graphite is minor. Diamond occurrence below the surface of the polished section, variable size and morphology and breakdown to graphite confirm the in situ origin. Coesite, with a thin rim of quartz, has been identified as an inclusion in kyanite which is itself completely enclosed in garnet, in one of the samples containing polycrystalline quartz aggregates. Thus the north Bohemian crystalline basement is an UHP terrane and it represents a fifth accepted location where diamond has been confirmed in situ in continental crust rather than mantle rocks (along with Kokchetav Massif, Kazakhstan; Saidenbachtal, German Erzgebirge; Rhodope Massif, Greece and Qinling Mts., China).

The microdiamonds have been found in both felsic quartzofeldspathic and intermediate garnet-pyroxene granulites from exposures in the Eger Crystalline Complex as well as drill cores in the crystalline basement c. 50 km to the ENE. The Saidenbachtal in Central Erzgebirge, belonging to the same Variscan unit, is located 50 km to NNE. Whereas the Saidenbachtal diamond-bearing gneiss is an unusual, rare rock [1], our granulites are macroscopically indistinguishable from those covering thousands of square kilometers of the Variscan crystalline core. Garnet peridotites are commonly associated with these granulites. Our discovery indicates that the continental crust was subducted deep into the mantle and captured slices of mantle thus finally yielding an explanation for the long known but still disputed granulite-garnet-peridotite association. Further, it suggests that the Variscan belt may be one of the largest UHP terranes worldwide.


The formation of organic molecules in solar system environments: The Miller-Urey Experiment in space preflight overview


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The Miller-Urey Experiment in space (MUE) will investigate the formation of prebiotic organic compounds in the early solar system environment when it is sent to, and later retrieved from, the International Space Station in 2012. The dynamic environment of the solar nebula with the simultaneous presence of gas, particles, and energetic processes, including shock waves, electrical discharges, and radiation may trigger a rich organic chemistry leading to organic molecules. Two gas mixture compositions (CH₄, NH₃, H₂ and N₂, H₂, CO) will be tested and subjected to continuous spark discharges for 48, 96, and 192 hours. Silicate particles will serve as surfaces on which thin water ice mantles can accrete. The experiment will be performed at low temperatures (-5 °C), slowing hydrolysis and improving chances of detection of initial products, intermediates and their abundances. Conducting the Miller-Urey experiment in the space environment (microgravity) allows us to simulate conditions that could have prevailed in the low gravity, energetic early solar nebula and provides insights into the chemical pathways that may occur as planetary systems form.

Mineralogical Magazine www.minersoc.org
Solute compositions and fluid residence times along an erosional gradient, Middle Fork of the Feather River, CA

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The residence time of water in the subsurface is known to be an important control on chemical weathering rates because longer contact times allow for waters to dissolve more minerals. A second control on weathering rates is erosion, which accelerates mineral dissolution by supplying fresh mineral to the soil environment from the bedrock below. However, on hillslopes erosion can also dramatically impact the hydrologic conditions. The rate of erosion may influence the slope of the terrain, the hydraulic gradient, and the amount of weathering products (e.g. clays and Fe-oxides). These effects result in shorter contact times and potentially decreased solute fluxes from rapidly eroding landscapes.

One conceptual model for assessing the relative importance of hydrologic and erosional processes is to consider the fluid residence time required to reach chemical equilibrium (which would determine the maximum solute flux) relative to the actual average fluid residence time of water in the hillslope. Weathering systems where these thermodynamic and physical time scales are closely matched should have the maximum rates of chemical denudation.

To test this model, we have studied the chemical and physical compositions of solids and waters from three soil-covered hillslope transects within a tributary basin of the Middle Fork Feather River, CA. One of the hillslopes is located above the knickpoint, while the others are adjacent to and below the knickpoint. Water contents and solute chemistry are fairly constant across each hillslope but variable between hillslopes. In general, the solute concentrations are lowest in the soils of the steeper hillslopes suggesting that water residence time is an important factor.

A new methodology to experimentally determine water incorporation into upper mantle olivine and pyroxene

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This study explores experimentally the incorporation of water in olivine and pyroxene near the solidus of fertile lherzolite compositions at 2.5 and 4 GPa. A sensor-layer of olivine or pyroxenes was added to both sides of lherzolite material and their water contents were determined by Fourier-transform infrared spectroscopy. The IR absorption bands of the sensor crystals after the experiment are different from the bands present in the starting material, indicating that the sensor minerals equilibrated with the lherzolite material. The similarity of absorption characteristics in experimental runs to those from mantle derived rocks (summarised in the PULI spectral database) indicates that hydrogen defects in the sensor minerals can be successfully reproduced in chemically complex systems. Olivine, orthopyroxene and clinopyroxene contain 30-190, 290-320 and 910-980 ppm of water under the studied P-T conditions. The partition coefficients between orthopyroxene and clinopyroxene (D_{opx/opx}) are 2.7 and 3.5 at 2.5 and 4 GPa respectively, while values of D_{ol/opx} are ~7 and ~5, at 2.5 and 4 GPa respectively. Olivine and pyroxenes in our water-rich experiments display higher water concentrations than what is documented for most peridotites. They overlap only with the most water-rich natural samples from supra-subduction environments. Our experiments reproduce closely water-saturated conditions in the upper mantle in chemically analogue complex systems. Thus, our experimental strategy may be generally applied in the future for mapping out phase relations and maximum effective water storage capacity of the upper mantle.
**Proxies for chemical weathering: Plio/Pleistocene red clay deposits from Hungary**

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**Introduction**

Red clays in Hungary (Tengelic Red Clay Formation: TRCF; Kerecsend Red Clay Formation: KRCF) is overlain by loess paleosol sequences. The red clay sediments in the Carpathian Basin are known from both exposures and boreholes. The age of these formations is ~3.5–0.5 Ma.

Nature of clay mineral assemblages is primarily a function of climate, essentially affected by the length of time of weathering, slope, water-rock ratio, and water chemistry. Therefore, clay mineralogy, and geochemistry are considered to be a powerful tool for interpreting weathering conditions and paleoclimate.

Elemental oxide analyses of red clays were determined by x-ray florescence (XRF), and x-ray powder diffraction (XRD) was used for mineral identification. In this study, we aim to determine the changes of clay minerals due to chemical weathering and age.

**Results**

The older type (Beremend Mb, age: 3.3–2.4 Ma) of the TRCF is red kaolinitic clay containing typically disordered kaolinite, mixed-layer smectite/kaolinite, smectite and little gibbsite. It was formed in the local subaerial weathering crust in warm, humid, subtropical or monsoon climate. The younger member of the TRCF (age: 2.5–1.0 Ma) contains red (or ‘reddish’) clay beds. It contains relatively fresh material (illite, chlorite), the weathering products are predominantly smectite and goethite formed under warm and dry climate in environmental conditions of savannah and steppe or forest steppe. The basal red clay layers of the Paks Loess Fm. and KRCF (age: 1.7–0.5 Ma) contain similar material as the underlying red clays belonging to the younger member of the TRCF. The slightly but significantly lesser degree of weathering (more illite and chlorite, less smectite) indicates cooling of the climate.

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**The epithermal deposits as a potential source of Critical High-Tech Metals (Ga, Ge, In, Sb)**

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In the recent evidences arise that some so-called ‘Critical High-Tech Metals’ of epithermal deposits are not only of academic interest. It is primarily concerns Sb and In which minerals in a number of deposits are appreciably accumulated. The IS-type epithermal deposits of Au-Ag-base metal usually accumulated in large of ore clusters (e.g. deposits Mexico, Peru, Romania, Serbia, Slovakia) can be considered as the potential source of Sb, produced by tetrhedrite - one of the main ore minerals. Some other deposits of this type (e.g. Tayoha, Goka in Japan, Prasolovskoe in Kunashir Island, Russia, etc) are enriched with In that is presented both, in the minerals (roquesite, sakuraiite, petrukite, and unnamed Zn-Fe-Ag-Cu-Sb-In-sulfides), and of high concentrations in sphalerite as well. In gold epithermal deposits of HS-type (e.g. Chelopech, Radka in Bulgaria) presence of Indium is provided mainly by high (to 4.7 wt. %) concentration in a sphalerite, unlike to rare roquesite. These and other similar deposits contain minerals of Ge (renierite, germanite, briartite, unnamed Cu-Fe-As-Ge-minerals) and Ga (gallite), as well. It is note, that considerable (to the first wt. %) concentrations of Ga are related to sphalerite too.

Thus contrary to existing conceptions that epithermal deposits mainly produce Au, Ag, as well as in some cases also Cu, Pb, Zn, some of these deposits already should be considered as byproducts sources of scarce rare, so-called Critical High-Tech Metals, such as Sb, In, Ge and, possibly Ga. While Sb, Ge, and Ga are more characteristic for IS-type deposits, In can accumulated in both types of epithermal mineralization.

This work was supported by ONZ RAS project 2-2 and RFBR project 10-05-00354.
Computation of Li equilibrium isotope fractionation between minerals and aqueous solution

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We present an efficient ab initio based computational method for prediction of the equilibrium isotope fractionation factors in the high pressure and temperature materials, including fluids. The method originates in the Bigeleisen and Mayer [1] approximation and requires only the knowledge of the force constants acting on the fractionating element. An important aspect of the proposed method is the explicit modelling of materials as continuous media. This allows for investigation of the expansion and compression effects, which influence the fractionation process in high -T and -P materials. We have tested our method by computing the Li isotope fractionation factors between complex Li-bearing crystalline solids (staurolite, spodumene and micas) and aqueous solution, and by comparison of the results with the existing experimental data [2]. We show that we are able to reproduce correctly the experimental isotope fractionation sequence: staurolite-fluid-mica-spodumene and reproduce the measured values within 1 ‰.

We also have investigated the predictive power of the widely used cluster approach, in which a fluid or solid is represented by a cluster of atoms and treated as a large molecule for derivation of the vibrational spectrum - the input for the computation of the equilibrium isotope fractionation factors. We show that representation of the aqueous solution by Li (H2O)n cluster results in the correct estimation of the isotope fractionation at low pressure (P<1GPa) but dramatically fails even on the qualitative level for higher pressures. This is because when computing materials under extreme conditions one has to account for the volume effects, such as compression or expansion, and structural changes in the fluid. These effects cannot be modelled unambiguously using the cluster approach. The proposed method accounts for these effects and predicts increase of isotope fractionation with pressure, which is more realistic and in agreement with the recent high pressure (P=8GPa) measurements for spodumene [3].


In situ δ18O and Mg/Ca analyses of diagenetic and foraminiferal calcite: Implications for paleoceanographic proxy records

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The vast majority of planktic foraminiferal shells in deep-sea sediments are affected by various degrees of diagogenesis; the effect on oxygen isotope ratios and minor/trace element abundances may be profound, but is debated. Previously, numerical models were applied to describe the oxygen isotope exchange during burial and recrystallization of deep-sea carbonate [1]. Furthermore, the partition coefficients for minor and trace element incorporation in diagenetic calcite are not clearly defined; in particular, the conversion of Mg/Ca ratios from diagenetically altered foraminiferal shells to water temperature is not straightforward.

We used an ion microprobe to analyze δ18O and Mg/Ca in 200-500 µm sized diagenetic calcite crystallites cementing small aggregates of foraminiferal shells from the Early Paleogene section of ODP Site 865, Central Pacific. The δ18O values of these diagenetic crystallites range from 0.1‰ to 2.2‰ [PDB] with an average of 1.2‰, and are in agreement with values predicted by numerical models [1]. The δ18O of these diagenetic calcites are ~6‰ higher than that previously reported from in situ measurements of unaltered domains (basal areas of muricae) within planktic foraminiferal shells from the same core samples [2]. Thus, both the endmember biogenic and diagenetic δ18O values are determined.

Mg/Ca of the diagenetic calcites range from ~25 to 100 mmol/mol with sharp gradients (variations of ~70 mmol/mol over 100 µm), implying complex, small-scale processes of dissolution and recrystallisation that are not reflected in the δ18O. The average Mg/Ca ratio of 60 mmol/mol confirms previous results from inorganic precipitation experiments [3] and is >10 times higher than the Mg/Ca of biogenic foraminiferal calcite. In contrast Mg/Ca ratios of diagenetically altered foraminiferal shells from the same core samples are not significantly elevated. Low Mg/Ca does not prove preservation of biogenic values because the processes governing foraminiferal diagene sis differ from those that mediate the precipitation of interstitial cements.

Mineral surface charge development in mixed electrolytes
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Electrolyte ions play a central role in electric double layer formation at mineral/water interfaces. The presence of these ions in aqueous solutions is in fact essential for neutralizing charges of potential-determining ions (H+, OH-) coordinated to mineral surfaces. The charge-neutralizing capacity of electrolyte ions is notably controlled by their size-to-charge ratio as well as their ability at forming or breaking water structures. Although much has been learned through the study of Hofmeister-type series of ions, understanding effects of co-existing ions at mineral/water interfaces is central to the elucidation of multicomponent systems representative of geochemical settings.

This study was devised to follow charge development on surfaces of \( \alpha - \) and \( \gamma - \) FeOOH submicron-sized particles in mixtures of NaCl and NaClO\(_4\) electrolytes. Surface charge and zeta potential data notably show that end-member NaCl and NaClO\(_4\) properties, such as capacitance and shear plane position, cannot be used to predict mixed systems (Fig. 1). Experiments on FeOOH particles of varied aspect ratios moreover point to important surface structural controls on these results as well. Mixed electrolyte systems are therefore likely to develop distinct interfacial water structures and ionic distributions.

**Figure 1**: Relative capacitances of synthetic goethite (\( \alpha - \) FeOOH) in mixed aqueous solutions of NaCl and NaClO\(_4\). Total ionic strength 0.1M Na(Cl, ClO\(_4\)).

Comparative genome analysis of *Metallosphaera yellowstonensis* and a novel iron-oxidizing sulfolobales from Yellowstone National Park
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Draft genomes have been completed for the iron and sulfur-oxidizing crenarchaea *Metallosphaera yellowstonensis* and Sulfolobales sp. strain MK5 (a novel member of the order Sulfolobales exhibiting only 89% 16S rRNA similarity to the closest *Sulfolobus* spp.). Both strains were obtained from a ferric iron mat within an acidic geothermal spring in YNP. This study compares the putative genes involved in iron and sulfur oxidation, heavy metal resistance, carbon fixation, and oxygen reduction between the two strains and with a diverse group of known iron-oxidizing acidophilic prokaryotes.

The draft genomes of each of these organisms contain sequences similar to putative iron-oxidizing open reading frames found in *M. sedula* and *S. tokodaii*, including a novel *fox* terminal oxidase gene cluster, a multicopper oxidase (*mco*), and the *cbs*AB-*sor*SN operon. These genes differ considerably from the hypothesized cytochromes found in the genomes of *Acidithiobacillus ferrooxidans* and *Leptospirillum* sp. Group II. *M. yellowstonensis* and strain MK5 contain conserved heterodisulfide (*hdr*) gene clusters believed to be involved in the oxidation of elemental sulfur, as well as sequences that code for proteins involved in the oxidation of sulfide (*sqr*), sulfite (*som*), and thiosulfate oxidation (*tqo*). Multiple copies of the heme copper oxidase (HCO) subunit I were identified in both draft genomes. *M. yellowstonensis* also contains a *bd*-type terminal oxidase not found in other known members of the Sulfolobales.

* M. yellowstonensis* and strain MK5 are similar to other Sulfolobales in regards to genes involved in CO\(_2\) fixation (i.e. 3-hydroxypropionate/ 4-hydroxybutyrate cycle) and heavy metal resistance; however, *M. yellowstonensis* is the only known archaeon to contain a methyl mercury lyase (*merB*) gene. Analysis of gene sequence data suggest that, in addition to the diversity of HCO’s, *M. yellowstonensis* and Sulfolobales strain MK5 exhibit novel mechanisms of iron oxidation, sulfur metabolism, autotrophy, and heavy metal resistance, all of which are consistent with the observed distribution of these organisms in high-temperature habitats of YNP.
Influence of different cleaning methods on seawater $\varepsilon$Nd extracted from planktonic foraminifera

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Seawater Nd isotope ratios extracted from foraminiferal calcite can be biased by contaminant phases, such as organic matter, ferromanganese coatings or secondary carbonates causing a shift towards bottom water signatures.

We compared two different cleaning methods to extract surface seawater neodymium isotope ratios from planktonic foraminiferal calcite. We used a modified version of the flow through method developed in [1] and a batch method following [2]. Single species samples (G. menardii and G. ruber pink) were obtained from core top sediments from the Gulf of Guinea to calibrate the method. Down core samples were investigated for paleoceanographic reconstruction of riverine input.

We tested the efficiency of two cleaning methods of the calcite by analysis of different element ratios (e.g. Al/Ca, Mn/Ca). The Al content was used as an indicator for successful clay removal whereas the Mn content reflects remaining early diagenetic coatings. Both elemental data and Nd isotope composition indicated indistinguishable levels of cleaning efficiency, whereby the batch method was less time consuming. For the different core top samples of our study clay particles had the strongest influence on the isotope and element ratios. To obtain a bottom water signature we analyzed mixed benthic foraminiferal carbonates from core top and down core samples. Additionally we compared these data with sediment leach data. The elemental ratios of the down core samples, both planktonic and benthic, showed elevated Mn/Ca ratios. To determine the origin of this contamination we analyzed the Fe/Ca and Mn/Fe ratios. The Mn/Fe ratios of planktonic and benthic samples presumably display different types of contamination.

In summary both planktonic and benthic foraminifera from the down core samples showed the same $\varepsilon$Nd values as the sediment leachates. Thus the Nd isotope composition of the foraminiferal carbonate has most probably been overprinted by the bottom water isotope composition.


Use of sequential extractions to evaluate the mobility of heavy metals in the Huanuni basin (Bolivia)

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Water and sediment quality in the Huanuni river basin is affected by acid mine drainage (AMD) from three main mines (mainly on cassiterite deposits). The area, with a population over 50.000 inhabitants approx., is located in the Oruro department, Bolivia. Concentrations of trace metals and REE were determined in stream waters, groundwater wells, suspended materials and bedload sediments. Moreover, a BCR sequential extraction (four-stage) were applied in bedload and suspended sediment in order to better constrain mobility and relative sources of trace metals and REE.

The main stream and tributaries waters are characterized by strongly acidic conditions (pH 2.9–4.5), elevated SO$_4^{2-}$ concentrations (up to 2400 mg/L), and high metal contents (especially Fe, Zn, Cd, Ni, Pb). Hydrochemistry coupled to sequential extraction allow the characterization of the contribution of the three considered main mines.

![Figure 1: Cu concentration and fractionation pattern](image-url)

The sequential extraction shows differences in partitioning and total concentration between suspended (in the figure indicated as codeaq, e. g HA3aq) and bedload sediment (e.g. HA3), with higher metal concentrations and exchangeable fraction in the suspended material. Cd, Zn and Cu (only Cu shown in Fig.1) seem related to the oxidizable fraction, whereas Cr and Ba with the reducible fraction.

Preliminary results suggest prioritizing remediation efforts on the suspended sediment.
Modeling of soil degradation in the Czech critical zone observatories

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Three small catchments situated 5-7 km apart, with similar forest cover (Norway spruce), but underlain by contrasting bedrocks served as critical zone observatories (CZO). Sites are situated in the geochemically diverse Slavkov Forest [1] close to power plants with large S emissions in 1950s - mid 1990s. The MAGIC model [2] was used to simulate soil and water chemistry. Model parametrization at Lysina (LYS, area 27 ha, podzol on leucogranite) and Pluhuv Bor (PLB, 22 ha, stagnosol on serpentinite) was based on published data [3]. Parametrization at Na Zelenem (NAZ, 55 ha, cambisol on amphibolite) was based on recent sampling [4]. Simulated soil base saturation (BS) declined from 20% to 6% at LYS, from 56% to 31% at NAZ, and from 94% to 88% at PLB (Fig. 1).

Figure 1: Simulated (lines) and measured (dots) soil base saturation at three Czech CZO in the Slavkov Forest.

Contrasting soil and drainage water compositions were generated mainly by differences in chemical weathering rates of divalent base cations, Ca and Mg (0.4 keq/ha/a at LYS, 1.5 keq/ha/a at NAZ, and 2.4 keq/ha/a at PLB).

Plant-microbe interactions in Cd-contaminated soils - Do Fe(III)-reducing bacteria influence the accumulation of Cd in the metal-hyperaccumulating plant Arabidopsis halleri?

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Soils worldwide have increasingly been contaminated with industrial waste metals, such as cadmium, which may subsequently enter the food chain through plants. These toxic metals can have dramatic effects on human and environmental health. Therefore, there is a need for the development and application of new techniques to efficiently remEDIATE contaminated soils. In the present study, we combined phytoremediation and (microbially) enhanced natural attenuation to determine whether a more time- and cost-efficient removal of cadmium from contaminated sites can be achieved. In plant-microbe-soil microcosms, geochemical and microbial parameters are determined to trace the microbial release of cadmium from Cd-bearing Fe (III) minerals by the natural microbial community of the soil or by an isolated Cd-tolerant Fe (III)-reducing bacterium. Additionally, cadmium uptake and accumulation by the metallophyte Cd hyperaccumulator plant Arabidopsis halleri in the presence of these bacteria is quantified. Cadmium is made phytoavailable to the plant by the stimulation of naturally occurring Fe (III)-reducing bacteria which release cadmium from Fe (III) (hydr)oxides through reductive dissolution. Subsequently, the aqueous cadmium is actively taken up by the plant A. halleri and accumulated in the above ground tissue. By harvesting the plant regularly, an efficient removal of cadmium from contaminated sites may be achieved.

Figure 1: Simulated (lines) and measured (dots) soil base saturation at three Czech CZO in the Slavkov Forest.

Calcium carbonate precipitation by the marine cyanobacterium *Trichodesmium*

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Cyanobacteria are important primary producers of the contemporary oceans and have affected global biogeochemical cycles over geological timescales. The diazotrophic *Trichodesmium* spp. are known for their large-scale blooms and substantial input of 'reactive nitrogen' to the oligotrophic subtropical and tropical areas. In this laboratory study, we monitored the buildup of biomass and concomitant shift in seawater carbonate chemistry over the course of a *Trichodesmium* bloom under different phosphorus (P) availability. During exponential growth, dissolved inorganic carbon (DIC) decreased while pH increased until maximum cell densities were reached. Once P became depleted, DIC decreased even further and total alkalinity (TA) dropped, accompanied by precipitation of aragonite. Under P-replete conditions, DIC increased and TA remained constant in the post bloom phase while no aragonite was formed. A diffusion-reaction model was employed to estimate changes in carbonate chemistry of the diffusive boundary layer of an aggregate of *Trichodesmium*. This study demonstrates that *Trichodesmium* can induce precipitation of aragonite from seawater and further provides possible explanations about underlying mechanisms.

Parental melts of Avachinsky volcano (Kamchatka) recorded in melt inclusions

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We studied ca. 700 melt inclusions (MIs) in 6 major minerals (Ol, Opx, Cpx, Pl, Amph and Mt) from 61 Holocene andesitic and basaltic andesites tephra of Avachinsky volcano erupted during the last 1014C ky.

Figure 1: MIs compositions in Avachinsky tephra depending on host mineral phase. Dotted line – compilation of MIs from island-arc rocks after [1].

MIs have low-K to middle-K basaltic to rhyolitic compositions (fig. 1). The continuum of MIs can be well explained by fractional crystallization from parental basaltic melts. No apparent bimodality is observed in the dataset in comparison with [1, 2]. Melts of intermediate compositions are abundant and commonly found in minerals from basaltic andesites. In comparison with the host rocks, MIs have systematically more silicic compositions, and this difference increases with increasing SiO2 content in the host rocks. Dacitic and rhyolitic MIs predominate in our dataset due to the prelevance of basaltic andesites and andesites on Avachinsky volcano.

These results show that the previously reported bimodality of MIs in island-arc rocks [1, 2] may result from unrepresentative sampling and does not reflect true volume proportions of melts with different SiO2 content in island-arcs.

Mantle peridotites from the Stalemate F.Z. (NW Pacific)

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The Stalemate Fracture Zone (SFZ) is a 500 km long SE-NW trending transverse ridge between the northernmost Emperor Seamounts and the Aleutian Trench, which originated by flexural uplift of Cretaceous (?) oceanic lithosphere along a transform fault at the Kula-Pacific plate boundary [1].

The lithosphere cropping out along the NW flank of the SVZ was sampled by dredging during the R/V Sonne cruise SO201-KALMAR Leg 1b. Strongly altered mantle rocks ranging from pyroxene-rich lherzolites and pyroxene-poor dunites were obtained at the station DR37 at the northern SVZ bend. The compositions of primary minerals (Cpx, Opx, Sp) change systematically from lherzolites to dunites. Sp in lherzolites has higher Mg#, NiO, lower Cr#, Fe3+ and TiO2 (Mg#=0.65-0.68, NiO=0.26-0.34 wt%, Cr#=0.26-0.33, Fe3+=0.021-0.030, TiO2=0.04-0.09 wt%) than spinel in dunites (Mg#=0.56-0.64, Cr#=0.38-0.43, TiO2=0.19-0.28 wt%, NiO=0.19-0.26%, Fe3+=0.027-0.043). Cpx in lherzolites is moderately Mg- and Ni-rich, Ti- and Na-poor, has lower Cr# (Mg#=91.7-92.4, Cr#=0.12-0.16, TiO2=0.06-0.15 wt%, Na2O=0.19-0.41 wt%, NiO=0.06-0.09 wt%) and is extremely MREE- and Zr-depleted (C1-normalized Yb=4.0-5.6, Sm/Yb=0.05-0.14, Zr/Yb=0.001-0.009) compared to clinopyroxenes analyzed in a sample of dunite DR37-3 (Mg#=93.7, Cr#=0.16, TiO2=0.23wt%, Na2O=0.85wt%, NiO=0.06wt%, Yb=5.7-7.4, Sm/Yb=0.22-0.27, Zr/Yb=0.22). Some Cpx from lherzolites have flattened or strongly U-shaped patterns of REE (Sm/Yb=0.11-0.49, La/Sm=0.36-3.6) though their major element composition is indistinguishable from the more LREE depleted Cpx.

The variations of Cpx and Sp compositions can be explained by the two-stage process [2]: 1) near fractional melting of depleted mantle to 10-12%, 2) interaction of the residual lherzolite with N-MORB-like melts to form dunites. The protolith of lherzolites and dunites dredged from the SFZ can thus represent disintegrated parts of shallow oceanic mantle variably modified by melt percolation.


Unusual apatite crystals and pegmatites with Rare Earth Elements tetrat effect

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Dolní Bory pegmatite deposit in the Czech Republic, display well developed zonality and different concentrations of rare earth elements with chondrite-normalized patterns that show a clear convex tetrat effect. Similar patterns and zonality exhibit also apatite crystals (Fig. 1). The Y/Ho and Sr/Eu ratios and very high Y and U content of the apatite samples correspond with evolved fractionation relative to the corresponding chondritic values. Based on the La/Lu, Sr/Eu and Y/Ho ratios of apatite, the apatite zones can be divided into two main groups which reflect two main stages of magma-fluid evolution, namely, a magmatic and a magmatic hydrothermal transition stage.

Figure 1: Chondrite-normalized REE profiles (apatite).

Interaction of a most evolved parental fluid with already formed pegmatite matrix and apatite probably produced the strongest REE tetrat effect in the youngest white zones of apatite rims (AZ3).

The variations of Cpx and Sp compositions can be explained by the two-stage process [2]: 1) near fractional melting of depleted mantle to 10-12%, 2) interaction of the residual lherzolite with N-MORB-like melts to form dunites. The protolith of lherzolites and dunites dredged from the SFZ can thus represent disintegrated parts of shallow oceanic mantle variably modified by melt percolation.

Deciphering the early fossil record of cyanobacterial mats based on their mode of mineralization

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Archean traces of life are vague and confusing due to poor preservation. Identifying traces of life in early geological record requires understanding the mode of fossil formation. Carbonaceous matter, although abundant in many Archean deposits, does not per se prove presence of life. Key to decipher earliest life forms could be their mode of mineralization. Etching of Neoarchean carbonates (Nauga Fm., South Africa) revealed coccoid cyanobacterial mats preserved as web-like structures composed of pits, mineralized with CaCO₃, and walls permineralized with Al-Fe-Mg-K silicates [1, 2].

Similarly permineralized web-like structures commonly occur in modern coccoid cyanobacterial mats. Studies on such mats from Lake Van (Turkey), Niuafo'ou Island (Tonga), and Satonda (Indonesia) showed that after death the mats undergo mineralization. The type of mineral phase(s) and the rate of mineralization depend chiefly on geochemical conditions within the degraded biomass. First to decompose is the cellular content and the thin mucilage sheaths surrounding individual cells and smaller groups of cells. Therefore cells are only exceptionally preserved. The most durable parts of the mat are the thicker outer web-like mucilagenous sheaths, which due to early permineralization with CaCO₃ and silicates, are fossilized.

Early diagenetic calcification and silicatization is associated with post mortem activity of heterotrophic bacteria. Bacteriolysis liberates cations complexed during cyanobacterial lifetime in their EPS. This process enhances mineral precipitation in the bacterially degraded mucilage sheaths and preserves their web-like texture. Morphology and mineral composition of Neoarchean web-like structures resemble those of modern mineralized cyanobacterial mats and can therefore be regarded as biosignatures of benthic coccoid cyanobacterial mats.


Density functional study of uranyl adsorption on solvated surfaces of clay minerals

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Actinide adsorption on clay mineral surfaces represents an important retardation mechanism for these metal ions. With the topical issue of safe disposal of radioactive waste in mind, it is important to gain comprehensive knowledge of the environmental chemistry of radioactive elements and their compounds, where the interaction of actinides with mineral surfaces in general plays an important role. Various experimental techniques are being used to examine these issues, and these results are favorably complemented by computational chemistry studies.

We explored uranyl adsorption on solvated clay minerals with the plane-wave based projector augmented wave approach as implemented in the program VASP. Neutral 1:1 layered kaolinite was considered as a simple model clay mineral. We focused on (001) basal aluminol and (010) edge surfaces. Solvation plays a crucial role when modeling the latter type of surfaces. These effects were approximated by including a mono- or bi-layer of adsorbed water in the quantum mechanical models.

We mainly explored bidentate inner-sphere adsorption complexes on deprotonated sites representing neutral or slightly higher pH. Uranyl adsorption on kaolinite edge surfaces commonly leads to a deprotonation of aqua ligands of uranyl, resulting in monohydroxide as adsorbate. Aluminol adsorption sites are preferable for uranyl adsorption compared to mixed aluminol-silanol sites. The geometry of adsorption complexes is compared to available experimental results. Overall, complex formation energies suggest that several adsorbed species may simultaneously be present at kaolinite surfaces.
Speciation and micro-scale spatial distribution of As in a mining-affected river floodplain

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Many rivers worldwide are polluted with trace elements originating from past or present mining. Even after closure and remediation of the mines, highly contaminated floodplains often remain as a source of contaminant release into river and ground water. Arsenic (As) has a high potential for mobilization under reducing conditions, e.g., during soil flooding, but this strongly depends on the speciation of As among other factors.

We studied the speciation and micro-scale distribution of As in alluvial soils and sediments along the river Ogosta in NW-Bulgaria. Ogosta, an important tributary to the lower Danube river, was strongly affected by mining of Au, Fe, and Pb/Ag between 1951 and 1999.

Soil samples were collected along transects ranging from the river bed through the lower and upper floodplains, taking special precautions to minimize oxidation. All samples were analyzed for soil pH, mineralogy, elemental composition, and oxalate-extractable As and Fe. Arsenic speciation was investigated by As K-edge X-ray absorption spectroscopy (XAS). Thin sections of undisturbed soil were prepared and examined by micro-X-ray fluorescence (µ-XRF) spectrometry and µ-XAS. Additionally, selected soils were size-fractionated to explore the elemental composition, mineralogy, and As speciation as a function of particle size.

Soil As concentrations in the floodplain ranged between 40 and 37,400 mg kg⁻¹. Highly As-contaminated soils were also enriched in Fe, Mn, S, Pb, Sb, and other trace elements. Bulk and micro-XAS, combined with oxalate-extractions, revealed that most As was present as As (V) sorbed to poorly-crystalline Fe (III)-oxyhydroxides, with smaller amounts of As bound in arsenopyrite. The fine particle size fractions <5 and 5-20 μm were strongly enriched in As (up to 93,000 mg kg⁻¹) as compared to the corresponding bulk soils. These size separates contained only traces of arsenopyrite and exhibited very high oxalate-extractable As and Fe contents, reaching molar Fe/As ratios of <5. Our results suggest that As and Fe in these soils should be readily bioavailable for microbial reduction upon soil flooding.

Groundwater Recharge in the Santo Tomás Valley, Baja California, México

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Overview

The purpose of this study is to better understand Mountain Front Recharge (MFR) and Mountain Block Recharge (MBR) in a mountainous watershed in Baja California by creating a detailed fracture-trace map of the Santo Tomas basin along with stable isotope (O, H) and chemical analyses of spring water (thermal and cold), groundwater, and stream runoff throughout the study area.

This study focused on the topography, geology, vegetation and hydrologic characteristics of the eastern section of the Santo Tomas valley, located approximately 50 km southeast of Ensenada. Each method used in study was completed with the intention to integrate all data to better understand MBR in the study area.

Methods

Models of elevation, slope, lithology, vegetation, and fractures within the 300 km² watershed were created to help characterize the basin. Images were generated in ArcMap, using DEM data, field observations, and LandSat satellite imagery. Each visual was examined individually as well as in conjunction with other physical and chemical parameters to better understand the dynamic of the watershed.

Results

The stable isotope (δ¹⁸O and δ²H) data show two distinct types of spring water within the watershed representing local and regional flow paths. Thermal springs, display a -1.9‰ δ¹⁸O depletion compared to the other spring water, indicating a higher elevations recharge or older waters. This distinct isotopic signal was found 15 km downstream in the alluvial aquifer, showing that a significant amount of water is recharging the basin aquifer via the mountain block along this flow regime. The thermal system and most cold-water springs surface along active faults, which appear to transmit more water than the undifferentiated fractures. An isotopic distinction can be seen between the hot and cold springs within the watershed despite that all the spring samples are taken between 400 - 550 m elevation.
Heavy minerals in the Kafue River sediments, Copperbelt Mining District, Zambia: Indicators of industrial contamination

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Sediments of the Kafue River that drains the whole of the Copperbelt region were found to contain up to 1 wt% Cu, 0.1 wt% Co, 1.3 wt.% Mn and a number of other toxic elements like Pb, As and Hg. The study of heavy minerals in both types of sediments was intended to identify the sources of contamination. Heavy minerals found in uncontaminated sediments of this river comprise mostly of ilmenite, limonite, rutile, amphibole and tourmaline, while apatite, clinochlore epidote and zinc are minor. On the other hand, the contaminated sediments contain, besides rock-forming minerals, chalcopyrite, pyrite, bornite, malachite and azurite the concentrations of which vary considerably. Chalcopyrite and pyrite evidently come from leaks of tailings still in operation in which the sulfides were not yet oxidized. Washing out and erosion of old flotation tailings ponds are responsible for enhanced contents of malachite, azurite, bornite, copper metal and chrysocolla together with limonite with high contents of copper and other elements in the contaminated Kafue River sediments. Particles of slag rich in magnetite and also particles of intermediate solid solution of Cu-Fe-S (ISS) affected by various degree of oxidation were found in sediments close to the smelters. The identification of heavy metals and their relative proportions enabled to assess the extent of contamination of stream sediments and also the character of individual sources of contamination. No extensive dissolution of copper and cobalt minerals in stream sediments takes place due to the neutral or slightly alkaline character of surface water in the area. However, occasional accidents in chemical plants processing copper and cobalt concentrate (acid spikes) result in short term but sharp increase in acidification of surface water (pH 3-4) which consequently leads to sharp increase in copper contents in these water. The study originated within the UNESCO/IGCP 594 Project ‘The impact of ore mining and processing on the environment and human health in Africa’.

Combining phase petrology, reaction balancing and partial pseudosections – Theory and examples

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Both classical phase petrology and phase diagram modelling by pseudosections have their strengths and weaknesses. Phase petrology is well suited for generic P-T grids and phase diagrams in relatively simple chemical systems or subsystems (e.g. KFASH in metapelites), but is hard to use in more complex systems, unless pure phases exist from which to project. Pseudosections [1, 2] are complementary to grids in portraying all reactions that may potentially operate in a given bulk composition as a function of P and T. Both petrological tools assume equilibrium conditions that may not always be appropriate. Reaction overstepping, re-entering of inclusions into a reacting assemblage during host breakdown, kinetic barriers, etc., all highlight the local absence of equilibrium or the operation of patchy equilibrium [3]. In addition, pseudosections assume constant bulk chemistry, which may be invalid during melt loss [2] and when certain phases (e.g. inclusions) or cores of zoned minerals do not participate in a reaction [3].

Hence, deriving P-T-t paths is a subtle process that requires a multi-faceted approach combining textural analysis, mineral chemistry, reaction balancing [4], qualitative pseudosections using model reactions [5], quantitative P-T pseudosections for selected microdomains, and thermobarometry on selected textures apparently close to equilibrium. In addition, P-T vectors may be constrained by modelling of reaction line slopes [6], a technique that merits far more attention and use. Examples are given from migmatites (Finland), granulites (Sri Lanka) and xenoliths (Spain) to highlight this approach.

Trace and REE geochemistry of the Angola Basin sediments

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We studied chemical composition of sediment core samples collected from the Angola Basin (23°30′S, 4°17′W, 4990 m depth). Oxidized pelagic foraminifera oozes (60-98 wt% carbonate) represent the recovered core (length 210 cm). Mn and reactive Fe concentrations range from 0.1 to 0.3 % and decrease with CaCO₃ increase. The contents of Co, Ni, Mo and U along the core correlate with Mn concentrations due to scavenging on Mn-oxyhydroxides. Concentrations of REE decrease with CaCO₃ content increase. The values of Ce-anomaly range from negative in carbonate-rich sediments to positive in the carbonate-depleted layers. The concentrations of REE and Th correlate with reactive Fe content (r > 0.9). REE pattern indicates its hydrogenous origin.

Using negative correlation of each rare earth and carbonate concentration (r > -0.9), we calculated REE compositions in 100% CaCO₃. The latter is consistent with REEs in Atlantic ocean foraminifera from Palmer [1]. REE pattern of red clay component was obtained by extrapolation to 0% CaCO₃, and coincide with mean composition of pelagic red clays from Brazil Basin located symmetrically across the MAR. The REE are originated from the two main sources: biogenic carbonate and red clay component, and could be defined with variable content of these constituents. Biogenic carbonate is characterized with Ce depletion and low concentrations of REE, red clay component has positive Ce-anomaly and higher concentrations of trivalent REE.

Volatiles in Siberian flood basalts: Melt inclusions study

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We report major, trace and volatile elements (Cl, F, B, S, H₂O) contents in melt inclusions in clinopyroxene phenocrysts from the Southern Maslovsky intrusion (Norilsk region) studied by EPMA, SIMS and LA-ICPMS technics. Modelling by PETROLOG software [1, 2] suggests that melts were saturated by both olivine (Fo 76-68) and CPX (Mg#78-69) and crystallized at shallow depth (below 100 MPa pressure) in the temperature range 1130-1080°C. Incompatible elements patterns of melts are similar to typical Siberian flood basalt (La/Smn=1.4, Nb/Lan=0.6, Gd/Ybn=1.1).

Melts are undersaturated by sulphur and have S/Dy=200, (150-300), markedly lower than for MORBs and OIBs (250-300, [3]). Water contents are variable (H₂O=0.08-0.45 wt%) suggesting low pressure degasing of melt. The highest concentrations yields H₂O/Ce over 160, close to the typical range of OIB and MORB [3]. Chlorine and boron show significant excess yielding Cl/K=0.29, (0.24-0.40); B/K=0.9*10⁻³, (0.6-1.2*10⁻³), which are few times higher than those for typical MORB and OIB [3]. Contents of fluorine F/Ti=0.045 (0.021-0.056) and F/Nd=29 (18-38) are also higher than commonly found in MORB and OIB [3].

The recovered accesses of Cl and B of SFB melt are very uncommon for intraplate mantle derived magmas. But they are similar to those of Gudchikhinskaya suit (one of the lower units of Norilsk volcanic section) parental melt, which was proposed as a pyroxenite-derived end-member component of SFB originated from recycled oceanic crust [4]. This may suggest that the recycled oceanic crust was one of the sources of excessive Cl and B in SFB in general. The other source could be the actual continental crust. Anyway, data suggest significant emission of Cl to atmosphere at the time close to P-T environmental crisis.

Murataite-pyrochlore complex oxide series for actinide immobilization: Nanoscale structure and complexity

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Synthetic murataite, an analogue of a rare titanate mineral, was identified in Synroc ceramic designed for immobilization of high-level nuclear waste [1, 2]. Five volume percent of this phase accumulated about 40% of the total uranium present in the sample. Laverov et al. [3] discovered different murataite varieties, Mu-3, 5, 7, and 8, where numbers correspond to the multiplicity of murataite a cubic unit cell parameter with respect to the same parameter of the fluorite unit cell. Experimental studies demonstrated that the crystallization sequence of phases in the U(Pu)Zr-Zr-Mo-Fe-Ti-Al-O system can be expressed as: Pyrochlore - Mu-7 - Mu-5 - Mu-8 - Mu-3. In murataite ceramic, typical grains contain pyrochlore and Mu-5 at the core surrounded by Mu-8 and Mu-3 phases. Since the most actinide-bearing phases are encapsulated by low-actinide varieties, this creates an additional barrier for actinide leaching and increases chemical durability of murataite ceramics. Recently, we have been able to structurally characterize Mu-3, 5, and 8 varieties of synthetic murataite and to demonstrate their polysomatic nature, in agreement with the earlier proposal by Urusov et al. [4]. It turns out that members of the murataite-pyrochlore series are the result of nanoscale mixing of murataite and pyrochlore structures. For instance, the structure of Mu-5 [5] is a complex framework consisting of pyrochlore unit cells uniformly distributed in murataite-type recombined structure. The structure of Mu-8 contains alternating murataite and pyrochlore unit cell modules separated by transitional structure.

The lamprophyre problem: Return to the roots

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The term ‘lamprophyre’ has been introduced in 1874 by Gümbel for Variscan mafic post-collisional dykes from the Bohemian Massif characterized by phenocrysts of mafic mica embedded in a feldspar groundmass (minette and kersantite type). In analogy to these, Rosenbusch in 1887 added the amphibole-bearing types such as vogesite and camptonite, from which spessartite was subsequently distinguished. Unfortunately, during the 20th century, petrologists enlarged this ill-understood group by incorporating different rocks containing mafic phenocrysts, such as kimberlites, lamproites, nepheline-, leucite- and melilite-bearing rocks. This resulted in a single large supergroup of polygenetic rocks termed the ‘lamprophyre clan’. In contrast, recent understanding of lamprophyres provides a sound basis for rejecting such a variable group of polygenetic origin [1, 2]. As true lamprophyres, we can now recognize five original types (end-members) among which there are continuous transitions: minette, kersantite, vogesite, spessartite and partly camptonite (in the original sense). It is important to note, that not every rock labelled as a true lamprophyre falls into this group. For example a ‘peralkaline minette’ is not a lamprophyre but very probably corresponds to a lamproite [c. f. 3, 4]. Since the term camptonite is usually used for an alkaline ‘lamprophyre’ variety (in fact volatile-rich basalt), I recommend not to use it in context with the true lamprophyres. Lamprophyre varieties containing kaersutitic amphibole can be easily described as titanospessartite or titanovogesite, respectively (Table 1). Moreover, the last proposed variety fills the gap in the current nomenclature.

Table 1: Proposed principal subdivision for the true lamprophyres. (Kfs = K-feldspar, Pl = plagioclase)

<table>
<thead>
<tr>
<th>Predominant mafic mineral with &quot;OH&quot; group</th>
<th>Al-undepleted phlogopite/biotite</th>
<th>Mg-hastingsite + others Ca amphiboles</th>
<th>kaersutite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kfs</td>
<td>minette</td>
<td>vogesite</td>
<td>titanovogesite</td>
</tr>
<tr>
<td>Pl</td>
<td>kersantite</td>
<td>spessartite</td>
<td>titanospessartite</td>
</tr>
</tbody>
</table>

Phlogopite/matrix, Cpx/matrix and Cpx/phlogopite trace element partitioning in true lamprophyres

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Introduction

Partition coefficients for true lamprophyres (i.e. in their original sense [1]) are poorly known. Therefore, mineral/matrix and mineral/mineral partition coefficients were determined by LA-ICP-MS for clinopyroxene (Cpx) and phlogopite crystals from a Variscan calc-alkaline (agpaitic index = 0, 6) lamprophyre of minette-type from the Bohemian Massif (Křižanovice locality, Bohemicum). Quantification was performed using the glass reference material NIST SRM 612 as external standard, and microprobe analyses of Si as internal standard.

Results

Cpx/matrix partition coefficients (D) for 23 trace elements have values ~1 (0.9-1.1) for the HREE only. This suggest that HREE can be concentrated in clinopyroxene during crystallization from lamprophyre melts [2]. The coefficients differ significantly from published D-values for HREE (~0.3-0.4) in clinopyroxenes growing from ‘lamprophyric’ melt of alkaline composition [3].

In phlogopite, only 14 elements had concentrations above detection limit. Phlogopite/matrix partition coefficients have average values higher than 1 for Ba (D = 1.1), Rb (D = 1.7) and Ti (D = 1.5). On the other hand, D-values for LREE are extremely low (D < 0.02) and it was not possible to determine D-values for the majority of HREE.

During simultaneous crystallization of clinopyroxene and phlogopite phenocrysts, Th, Zr, Hf and REE are preferentially partitioned into clinopyroxene. The main reason for the behaviour of these elements may be found in the lack of a suitable crystallographic site in the phlogopite structure [5].


Chronology of climate archives – A never-ending story

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Accurate dating of climate archives is essential for the reconstruction of past climate and to infer rates of climate change. Of special interest is the time range of the last Glacial and the transition into the Holocene, during which strong climate fluctuations are evident. Chronology of these archives is based on a number of dating systems, such as radiocarbon, U/Th and layer counting. Each clock has its strengths and limitations, and in the past decade important progress has been achieved to resolve inconsistencies within a dating method and between the methods. This keynote lecture will focus on this fascinating venture and the current status of establishing firm and consistent chronologies in the past 50,000 years.
O-isotope compositions of ferroan olivine in Ngawi (LL3–6) breccia
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Ferroan olivine (fa, Fa_{50-99}) is one of the major minerals in matrices of unequilibrated ordinary (H, L, LL) and metamorphosed carbonaceous (CV, CK, CO) chondrites. The origin of matrix fa is not understood: high-T (>1000°C) gas-solid condensation under highly oxidizing conditions in the protoplanetary disk [1–3] and low-T (<300°C) formation during fluid-assisted thermal metamorphism on the chondrite parent bodies [4, 5] are being discussed. Here we report on the mineralogy and O-isotope compositions of secondary fa (Fa_{50-99}) in LL3 clasts of the Ngawi LL3–6 breccia. The fa coexists with phyllosilicates, replaces magnetite+sulfide nodules in chondrules and matrix and forms veins crosscutting fine-grained rims around chondrules. On a three-isotope diagram, oxygen compositions of fa measured in situ using the UH Cameca ims-1280 plot along mass-dependent fractionation line with \( \delta^{17}O \) value of 4.2±1.4‰ (2σ), well above the compositions of phenocrysts in LL3 chondrules [7].

The similar \( \delta^{17}O \) values, 4.9±1.9‰ (2σ), were reported for magnetite grains in Ngawi and Semarkona (LL3.0) [1]. We conclude that Ngawi fa formed in situ in the presence of aqueous solutions.

Late Cretaceous alnöite from the Delitzsch (Germany) carbonatite – ultramafic complex
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The Delitzsch complex consists of late Cretaceous ultramafic lamprophyres, alnöites and carbonatic rocks, which are covered by up to 100 m thick sequences of Tertiary sedimentary rocks. Lamprophyre, alnöite and carbonatic dikes and diatres are emplaced in Paleozoic to lower Permian volcanic and sedimentary rocks. The size and geometry of the Delitzsch complex is not well known, but exploration drilling has documented lamprophyres and carbonatites in an area of 150 km² [1]. The complex includes a diversity of magmatic and subvolcanic rocks, ranging from beforites, rauhaugites, and alvikites for the carbonatic rocks and aillikites, monchiquites, alkali picrites, and alnöites.

Contact relations and distribution of xenolithic material indicates that phases of carbonatite and ultramafic lamprophyre magmatism overlapped.

The alnöite dike/diatrem at the northern flank of this complex is highly heterogenous with abundant wallrock xenoliths and reaction zones between alnöite and xenolithic material. The xenolithic material was incorporated during ascent and emplacement of the alnöite. Fresh alnöites have abundant melilithe, minor olivine, phlogopite, and pyroxene in a porphyritic texture. Accessory minerals are perovskite, apatite, chromian spinel, and magnetite. They are affected by post magmatic chloritization of olivine and especially pyroxene. The alnöites are relatively high in SiO₂ (~35%) and have high MgO, Cr, Ni, and Sr contents. The rocks have unradiogenic Sr and positive \( \epsilon^{Nd} \) (T) values. Their Sr, Nd, and Pb isotopic compositions fall between HIMU and EM1 mantle components.

Xenolith-bearing alnöites show separated areas with rounded quartz and K-feldspar. These texturally distinguished types are also geochemically and isotopically distinctive, with REE pattern similar to average crust and crustal Sr, Nd, and Pb isotope signatures. Xenolith-bearing alnöites show texturally and geochemically marked transition zones with selective enrichment of heavy REE, not attainable by simple assimilation of xenolithic material in the alnöite.

Microbial conversion of oil, coal and shales into methane –
A future energy resource

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Since decades it is known from stable isotope studies that large amounts of biogenic methane are formed in oil reservoirs. The investigation of this biodegradation process and of its biogeochemical controls are of great economical and social importance for: (1) The understanding of reservoir biodegradation may be of great use for the exploration industry, and (2) a biotechnological stimulation of methane formation in reservoirs could provide new economical perspectives for hydrocarbon recovery. Even under optimal conditions, today not more than 30-40 % of the total oil in a reservoir are actually recovered. The conversion of at least parts of the non-recoverable oil, coal or shales via an appropriate biotechnological treatment into easily recoverable methane would provide an extensive and ecologically sound energy resource. Laboratory mesocosms and high pressure autoclaves with samples from different geosystems showed high methane production rates after the addition of different oils, coals or shales. Stable isotope probing (SIP) combined with fingerprinting of the microbial enrichments showed a large bacterial but limited archaeal diversity involved in degradation. For the characterization of degradation pathways metabolite spectra will be analysed, combined with the use of SIP. The variability of carbon and hydrogen isotopes of produced methane falls in a relative narrow range. Further we have analysed the isotope composition of methane in reservoirs and oil-contaminated aquifer to test whether the isotope composition of methane can be used as an indicator for methanogenesis. The variability of carbon and hydrogen isotope composition in situ was almost identical with those obtained with the enrichment cultures. This implies a common methanogenic degradation mechanism resulting in consistent patterns of hydrocarbon alteration. This will provide an exploration tool to identify and assess these microbial processes in different reservoir geosystems. Mass balance calculations showed that significant fractions (2-10%) of added coals or oils were converted to methane. Current studies focus on the identification of stimulating or inhibiting factors for scale-up and field studies on MEOR.

Fluid inclusions in stalagmites used as a quantitative thermometer in paleoclimate research

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We present a new approach to determine paleo-temperatures (mean annual surface temperatures) based on fluid inclusion liquid-vapour homogenisation temperatures ($T_h$) in stalagmites. A precondition for these measurements is to stimulate the nucleation of a vapour bubble in the initially monophase inclusions by means of single ultra-short laser pulses [1]. The aim of our study is to explore the potential and the limitations of this new paleothermometer and to develop a reliable methodology for routine applications in paleoclimate research. Therefore, we have investigated recent fluid inclusions from the top part of actively growing stalagmites from various caves to compare our results with the present-day cave air temperatures.

The method makes specific demands on the selection, handling and preparation of the stalagmites to avoid artificially induced modifications of the original fluid densities by leakage or stretching of the inclusions. Additionally, the measured homogenisation temperatures $T_h$ (obs) need to be corrected for the effect of surface tension to determine the nominal homogenisation temperature $T_h$ (nom) [2] that is expected to be equal to the stalagmite formation temperature and therefore closely corresponds to the mean annual surface temperature outside the cave. Based on our present results we may expect an accuracy in paleotemperature determinations within ±0.3 °C. The application of this thermometer is, however, restricted to climate zones and periods with mean annual surface temperatures higher than 9–11 °C. Inclusions formed below this temperature limit do not feature a stable liquid-vapour state and thus $T_h$ cannot be measured.

Hf-W evidence for rapid accretion and core formation in protoplanets

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Introduction

Several Hf-W studies [e.g. 1] showed that the parent bodies of magmatic iron meteorites formed very early, about contemporaneously to Ca-Al-rich inclusions (CAI). Cosmic-ray induced neutron capture reactions can, however, modify the W isotope budgets of iron meteorites [2] but no accurate method is yet available for correcting these effects [3 , 4]. Consequently, the exact timing and duration of core formation in these bodies remain uncertain.

Approach

Cosmogenic noble gas abundances can help to select iron meteorite samples whose W isotope budgets likely remained unaffected by cosmic rays. Nevertheless, quantitative corrections of cosmic-ray induced shifts in W isotopes using a direct neutron dose monitor like 113Cd [see e.g. 5] are desirable [2]. We here report results from a combined noble gas and W isotope study on different groups of magmatic irons. Complementing Cd isotope analyses on the same samples are currently on going.

Results

Cosmogenic noble gas concentrations in most of the analyzed samples are at the lowermost end of the range observed in iron meteorites [6]. Samples with the lowest cosmogenic noble gas abundances have ε182W values (10^4 deviations from the terrestrial value) ranging from -3.3 to -3.2, indistinguishable from the CAI initial of -3.28±0.12 [7].

Implications

The (weighted) mean ε182W of the weakly irradiated irons analyzed in this study is -3.25±0.05. Unlike in previous W isotope studies, this average value is higher than the CAI initial, not lower, demonstrating that ε182W values lower than the CAI initial reflect cosmic-ray induced effects. Our W isotope data indicate that different iron meteorite parent bodies segregated their cores within a brief interval of less than 1 Myr. The average core formation age of the samples investigated here is 0.3±1.3/1.1 Myr after Solar System formation.

δ¹⁸O and Cl/Nb evidence for fractional crystallization origin of silicic island arc magmas
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Subduction-related silicic magmas may form either by extreme crystal fractionation or by partial melting of crustal rocks. Both mechanisms can be distinguished by their characteristic δ¹⁸O and Cl signatures.

Laser-fluorination analysis of andesitic to rhyolitic volcanic glasses from the Kermadec island volcanoes and of basaltic to dacitic glasses from the Lau and Havre backarc rifts yielded very uniform δ¹⁸O values of 5.4 to 6.5‰. This range is characteristic for mantle-derived magmas. The Cl concentrations show a positive correlation with the SiO₂ content while Cl/Nb ratios remain almost constant for the samples.

Magma generation by partial melting of sediments and/or low temperature hydrothermally altered oceanic crust, both typically having high δ¹⁸O, can be ruled out as these processes would cause much heavier isotopic values. A strong positive correlation between δ¹⁸O and SiO₂ content would be expected but is not seen in our data.

Hydrothermal alteration of the oceanic crust leads to amphibolite with low δ¹⁸O, and melting of such rocks would lead to values much lower than observed. Assimilation of such materials also causes high and variable Cl concentrations and variable Cl/Nb ratios unlike the observed systematic trend.

The small variation of the δ¹⁸O data as well as the very slight increase with SiO₂ content is best explained by fractional crystallization that modifies δ¹⁸O values of the precursor mantle magma by 0.3 to 0.8‰ towards heavier values [1]. This is also consistent with a positive correlation between the incompatible Cl and SiO₂ content and with the constant Cl/Nb ratios in these samples. Both parameters prove monotonous enrichment of the magmas in Cl with increasing differentiation and indicate that degassing was insignificant at least for the submarine glasses.


Destruction of Paleoproterozoic crust: Deciphered from detrital zircon populations and geochemistry of quartzites (NE Poland)
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Among the many crystalline rocks sampled from the Precambrian basement of NE Poland, which is accessible only by drilling, there are local occurrences of quartzites and quartzitic schists. The quartzites were previously interpreted as Neoproterozoic quasi-platform cover which was formed during post-Gothian peneplanation after emplacement of Mezoproterozoic AMCG intrusions [1]. Correlation with Jotnian sediments exposed in Central Fennoscandia (Baltic Shield) was presumed. Here we present the first results of detrital zircon U-Pb and geochemical investigations of the provenance of quartzitic samples from two isolated drill holes (Mokit and Zabiele). Quartz meta-arenites and subarkoses in terms of Herron’s chemical classification record a transition from an active continental margin towards a passive continental margin setting (Th–Sc/Zr/10, Th–La–Sc and Ti/Zr–La/Sc plots). A total of 70 detrital zircon grains from two drill core samples were analyzed by SHRIMP II. The U-Pb data demonstrate that the detritus was derived mainly from Paleoproterozoic crust (2.1–1.8 Ga). Archean grains are rare. No Mezoproterozoic component was detected. Three Paleoproterozoic age populations were identified with a major peak at 1.95 Ga. The youngest concordant grains were dated at 1757 ± 24 Ma (Mokit depth 740 m) and 1745 ± 24 Ma (Zabiele depth 690 m) age. These data, however, do not support a Jotnian signature as deposition of Jotnian sediments in central Fennoscandia continued long after the 1.55 Ga anorogenic rapakivi magmatism up to 1.26 Ga A significant revision of the formerly assumed stratigraphic position of quartzitic rocks and correlation with uppermost mature Paleoproterozoic Västervik quartzites [2], S Sweden from the Fennoscandian continental margin, is proposed.

Geochemistry of tin in the southern part of the Silesian Upland

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Introduction

Majority of soils from the southern part of the Silesian Upland are highly degraded and contain elevated levels of the toxic heavy metals [1]. Therefore, the purpose of presented studies was evaluation of tin pollution and determination of its mobility and bioavailability in soils from the investigated area.

In this work the soil samples were taken from industrial area. The soils samples were collected from two depths: topsoil (0, 0-0, 3 m) and subsoil (0, 8-1, 0 m). Comparison of elements concentration between topsoil and subsoil allows identification of the source of pollution (natural or anthropogenic).

Results

Considerably degree of chemical degradation was observed in both types of analyzed samples. The subsoil and topsoil samples were rich in tin (subsoil – 1265 mg/kg, topsoil – 37 mg/kg). Moreover, in both samples were noticed high concentration of copper, mercury, lead, arsenic and sulphur.

The sequential extraction experiments according to BCR method [2, 3] showed minimal tin mobility in the analyzed samples (almost 99% of tin was leached in the 4th step with aqua regia). The X-ray diffraction (XRD) analysis of selected samples showed the lack of tin minerals in the investigated soil. However, found the presence of quartz, clay minerals, calcite and gypsum.


Mesoarchean gabbroanorthosite magmatism of the Kola Region (Russia)

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The Kola peninsula is the region marked with development of anorthosite magmatism in the NE Baltic Shield. The Archaean gabbroanorthosites intrusions - Tsaginsky, Achinsky and Medvezhe-Schucheozersky - have the age of 2.7-2.6 Ga. The Patchemvarek and Severny gabbroanorthosites intrusions are located in the junction zone of the Kolmozero-Voronja greenstone belt and the Murmansk domain. Age data for sedimentary-volcanogenic rocks of the Kolmozero-Voronja belt and Murmansk domain granitoids are 2.8-2.7 Ga.

The gabbroanorthosites intrusions have more calcic composition (70–85% An) of normative plagioclase, and low contents of TiO₂, FeO, and Fe₂O₃. U–Pb zircon dating established Mesoarchean ages of 2925±7 and 2935±8 Ma for the gabbroanorthosites of the Patchemvarek and Severny massifs, respectively. The gabbroanorthosites of the studied massifs have fairly low REE contents (Ce₀ = 2.2–4.2, Yb₀ = 1.6–2.6) and distinct positive Eu anomaly. Comagmatic ultrabasic differentiates have practically unfractionated REE pattern, low total REE contents (Ce₀ = 1.2, Yb₀ = 1.1, La/Yb₀ = 1.32), and no Eu anomaly. The studied samples of the Archean gabbroanorthosites are characterized by positive εNd = +2.68 for the gabbroanorthosites of the Severny Massif and from +2.77 to +1.66 for the Patchemvarek Massif. The rocks of the Severny and Patchemvarek massifs have ⁸⁷Sr/⁸⁶Sr = 0.70204±8 and ⁸⁷Sr/⁸⁶Sr = 0.70258±8, respectively. The differences in the initial ¹⁴³Nd/¹⁴⁴Nd ratios between the Neoarchean and the Mesoarchean gabbroanorthosites suggest the existence of two mantle sources. One of them produced intrusions with an age of 2.67–2.66 Ga, while other was responsible for the formation of massifs with an age of 2.93-2.92 Ga.

The gabbroanorthosites of the Patchemvarek and Severny massifs were presumably derived from MORB-type basalts of oceanic settings, while the Tsaginsky, Achinsky, and other anorthosite massifs of the Neoarchean age were generated from subalkaline magma formed in within plate anorogenic setting. The Sm-Nd isotope data suggest the existence of several mantle sources in the Kola region, which produced melts for different-age gabbroanorthosite massifs since Mesoarchean to the middle Paleoproterozoic.
In this study, chemical and mass changes of Çetilli (Ordu) area vein type mineralization at the Eastern Black Sea region are investigated. The geology of the study area consists of volcanic, sedimentary and intrusive rock units. The study area is covered by Upper Cretaceous aged andesite, basalt and their pyroclastic equivalents, trachyandesite and its tuff, volcano-sedimentary sequence and limestone; Paleocene aged limestone, sandstone, claystone, marl, tuff and andesitic dyke; Eocene aged nummulites bearing limestone, andesite, basalt and their pyroclastics, monzonite; Upper Eocene aged basalt and Quaterner aged travertine. Upper Cretaceous aged andesite, basalt and their pyroclastics are cut by E-W, NE-SW, NW-SE directed many fault systems. The Çetilli Orebody was formed by hydrothermal solutions arising throughout this fractured and cracked zones. Ore minerals are pyrite, sphalerite, chalcopyrite, galena and nabit gold.

Alteration of Çetilli Mineral Deposit display indistinct spatial zonation. Alteration zones are completely controlled by fault systems. Alteration types are observed silification, calcification, zeolitization, clay, sericitization, limonization, hematization and pyritization. Chloritization and epidotization are observed cut distal part of veins. Alteration minerals are mainly quartz; lesser calcite, dickite, nacrite, ankerite, dolomite, kaolinite and a bit barite. The mass change calculations indicate a 19% volume increase in the ore zones, mainly due to addition of Si (24.45g/100g), Ca (1.06g/100g), K (0.61g/100g) and ore forming elements.

Comparison of internal and external metabolites produced by a diatom

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Methods

We sampled laboratory cultures of a marine phytoplankton (Thalassiosira pseudonana) at different stages of its growth. At each sampling point, we compared the molecular-level composition of dissolved organic matter released into the environment with the dissolved organic compounds retained within the phytoplankton cells. All measurements were made with an HPLC coupled to an ultrahigh resolution mass spectrometer (FT-ICR MS) in positive ion mode. Resulting mass and fragmentation data were compared to metabolite databases such as KEGG and MassBank.

Results

Our data reveal distinct differences between the dissolved organic compounds retained inside the phytoplankton compared to those compounds released into the surrounding media as well as some similarities in these two metabolite pools. Tentative identifications based on database comparisons and fragmentation data suggest a dynamic metabolome for T. pseudonana. From these identifications, we will present possible biomarkers for future quantitative metabolic studies of this diatom and related organisms.

Evolution of Variscan orogenic Popiel peridotite (SW Poland)

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Small (few hundred metres in diameter) outcrop of peridotite occurs in the western part of the Sudetes (SW Poland) at the Intra-Sudetic Fault Zone, close to the NE margin of the Karkonosze granite, which is one of the main tectonic lines in NE Bohemian Massif.

The rock consists of olivine (Fo_{84-88}, NiO 0.17 – 0.36 wt %), orthopyroxene (mg# 0.84 - 0.88, Al_{2}O_{3} 0.71- 4.69 wt %) and spinel (typically Mg_{0,68}Fe_{0,31}Ni_{0,01}Al_{1}, γFe_{0,13}Cr_{0,08}Al_{0.79}Fe_{0.13}Cr_{0.19}Al_{0.06}Ti_{0.03}O_{4} + chromiferous magnetite (Fe_{1.99}Mg_{0.02}Mn_{0.01}Ni_{0.01}Fe_{1.68}Cr_{0.19}Al_{0.06}Ti_{0.03}O_{4} + very scarce ilmenite. The composition of minerals vary from sample to sample. The primary mineral assemblage is overprinted by tremolite (Si = 7.95 atoms pfu), overgrown by magnesiohornblende (Si = 6.78 a pfu). The serpentine is texturally later than the amphibole.

The rock composition: SiO_{2} 39 - 43, Al_{2}O_{3} 4 – 7, CaO 3- 6 wt %, MgO 24 – 32 wt % and FeO 11 -13 wt % is Fe, Al and Ca enriched. Whole rock trace-element and REE patterns are slightly (1 – 10 times) enriched relative to primitive mantle, flat, with weak Zr and Eu negative anomalies. The rocks was altered by low-grade metamorphism producing tremolite, followed by contact metamorphism in the Karkonosze granite aureole (hornblende crystallization). The rock has been affected by metasomatism and later metamorphism under oxidizing conditions. It is the unique in Sudetes (NW margin of the Bohemian Massif) example of small orogenic peridotite body affected by metasomatic and metamorphic conditions.
On the application of jarosite and hematite thermochronology to assess aqueous environments on Mars

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Hematite and jarosite, identified in the Burns Formation by the Opportunity Mars Exploration Rover (MER), have been interpreted as in situ evidence for past aqueous conditions on the Martian surface. Hematite has been demonstrated as a useful (U-Th)/He chronometer, although it is not a commonly analyzed mineral. Likewise, jarosite has been used as a $^{40}$Ar/$^{39}$Ar chronometer, although prior to this study, argon diffusion kinetics in jarosite were unknown. Using long-duration, low-temperature, furnace step heating, jarosite argon diffusion parameters ($E$, log $D_0/a^2$) have been determined. Incremental fractional loss measurements from three size fractions (75-125, 125-150, 150-200 µm) yield an average activation energy (E) of 38.80 ± 1.58 kcal/mol and a log $D_0/a^2$ ± 0.67 s$^{-1}$ corresponding to a closure temperature (cooling rate 100°C/Myr) of 146 ± 30°C. Using published morphologic constraints and He diffusion kinetics on hematite spherules, and newly determined argon diffusion parameters for jarosite, we use the forward modeling program DECOMP to assess if these minerals will retain original (U-Th)/He and $^{40}$Ar/$^{39}$Ar ages during long residence times (4.0 Ga) at Martian surface conditions (22°, 0°C). Model results indicate that for hematite spherules (≥1.0 mm in diameter), (U-Th)/He and $^{40}$Ar/$^{39}$Ar ages will record the timing of formation within analytical certainty. Jarosite (75-200 µm in diameter) is also expected to retain radiogenic $^{40}$Ar, with predicted ages falling within 0.5% of the true age. We infer that in the absence of post-crystallization diffusive He or $^{40}$Ar loss, (U-Th)/He and $^{40}$Ar/$^{39}$Ar ages measured from Martian hematite spherules and jarosite respectively, can be used to constrain the time since water was present on Mars. Application of model results to the ‘wetting-upwards’ Burns Formation at Meridiani Planum, indicates that post depositional hematite from the lower eolian dune subunit would provide a minimum age of deposition, while possibly syndepositional hematite from the upper interdune/playa unit may yield the age of the unit. Jarosite ages throughout the section should record a downward migrating aridification front as the water table retreated. A vertical profile of hematite and jarosite thermochronology to samples returned from Mars may be key to determining if water was available for sufficient durations required for the development of life.

Rhine River: First case of anthropogenic lanthanum as a dissolved microcontaminant in the hydrosphere

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The rare earth elements (REE) are a group of elements that behave coherently in natural systems, usually plotted with concentrations normalized to a known reference (e.g. shale). This style of representation makes the presence of anomalies easier to distinguish.

The first report of anthropogenic contamination of the natural REE distribution in river water appeared in the mid-1990s (Bau & Dulski, 1996). Gadolinium (Gd) concentrations in the Havel River downstream of the city of Berlin were up to 3 orders of magnitude higher than natural background concentrations. This study also reported on the Rhine River showing a similar excess of Gd concentration. Gadolinium is used in magnetic resonance imaging as a contrast agent, causing positive anthropogenic Gd anomalies in sewage effluent, rivers, estuaries and groundwater via several pathways in its highly-stable form (e.g. Gd-DTPA).

More recently, excess lanthanum (La) was also measured in the River Rhine, up to an order of magnitude higher than background values. The anomaly is introduced into the Rhine River north of the city of Worms at Rhine river-km 447.4. Samples taken a few hundred meters upstream/downstream of an effluent at this location show strong differences in La and light REE concentrations. The effluent itself shows 49 mg/kg La, well-above levels that are ecotoxicologically effective. Excess La is present 400 km downstream at the German-Dutch border where >93% of total La and Gd are of anthropogenic origin.

Since River Rhine water is used for artificial groundwater recharge and bank infiltration, anthropogenic La (and Gd) are both to be expected in tap water of those cities that rely on the Rhine River as a drinking water source. Indeed, several cities along the Rhine River carry positive anthropogenic Gd anomalies (e.g. Leverkusen, Koblenz, Düsseldorf, Duisburg, and Essen) and positive anthropogenic La anomalies (e.g. Leverkusen, Worms, and Kleve).

While several adverse health effects of Lanthanum are known, information on the potential health risks to the ecosystem inhabiting the river is lacking. Further research and monitoring is essential in order to avoid potential negative environmental consequences.
Risk assessment analysis of Kadji-Sai uranium tailings site, Kyrgyzstan

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Sediment samples and coal ashes from Kadji-Sai uranium tailing site, Kyrgyzstan (a former coal and uranium mine) taken at depth of 0.1-0.2, 1, and 2 meters were investigated with gamma spectrometry and electron microscopy coupled with Energy-Dispersive X-ray Fluorescence Spectroscopy (SEM/EDX). Gamma spectroscopy showed significant elevated activities for uranium, radium, and lead-210 (Table 1).

<table>
<thead>
<tr>
<th>Sampling points</th>
<th>Depths (m)</th>
<th>238U kBq kg⁻¹</th>
<th>226Ra kBq kg⁻¹</th>
<th>210Pb kBq kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catchment pool</td>
<td>0.1-0.2</td>
<td>0.43 to 1.2</td>
<td>0.10 to 0.07</td>
<td>0.11 to 0.07</td>
</tr>
<tr>
<td>Uranium tailing dump</td>
<td>1.0</td>
<td>6.8</td>
<td>31.2</td>
<td>23.9</td>
</tr>
<tr>
<td>Uranium tailing dump</td>
<td>2.0</td>
<td>7.2</td>
<td>26.6</td>
<td>24.2</td>
</tr>
</tbody>
</table>

Table 1: Gamma activity at shallow depths of the Kadji-Sai uranium tailing site

These results reveals that the uranium extraction technique was rather inefficient leaving about between 20 and 30% of the uranium in the tailings and that no sufficient cover of the tailings is in place. SEM/EDX was used to study the chemical forms and morphology of the coal ash and sediments particles. The precise knowledge of the elemental composition of radioactive wastes occurring in the tailings is important for future remediation and migration of radioactive elements and stability of secondary minerals being formed in the dump piles.

Figure 1: SEM image and EDX data of coal ash from different depths

Consistent treatment of entropy, enthalpy and volume effects of multi-dentate adsorption reactions

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Evidence for aqueous ions binding to several oxygen atoms on mineral-water interfaces (MWI) has raised interest in multi-dentate surface complexation models [1, 2]. We investigated [3] how (fitted) intrinsic equilibrium constants [\(\times\)] for \(\delta\)-dentate M adsorption reaction depend on the choice of concentration scale for \(\#\)M, e.g. molarity (\(\theta\)); relative surface fraction (\(\phi\)); molecular surface density (\(\sigma\), in mol·m⁻²); or relative surface density \(\Gamma\) (\(\sigma\), where \(\Gamma = 2 \times 10^{-5}\) mol·m⁻² [4]). We have shown that, for \(\delta \geq 2\), only \(\times\) and \(\phi\) are denticity-invariant, and only \(\times\) is independent of the real site density \(\Gamma\). This makes \(\times\) the (*) scale the best choice for defining the standard state of a surface species.

In this contribution, our approach is extended to \(T\) and \(P\) corrections of \(\times\) defined by the partial molar entropy \(\Delta S\), enthalpy \(\Delta H\), isobaric heat capacity (\(\Delta C_P\)), and volume \(\Delta V\) effects (at \(T = 298\) K) of the M adsorption reaction. These effects can be predicted, or fitted from \(\times\) values known for several temperatures. For the same experimental data set, fitted \(\Delta S\) values depend on the chosen concentration scale for \(\times\); the bias can reach 275 K·mol⁻¹ for tetradentate cations on rutile surface. General conversions such as

\[
\Delta_{\#M}^\phi S_{\text{M,298}}^\phi - \Delta_{\#M}^\phi S_{\text{M,298}}^{\text{surf}} = -R(\delta - 1)\ln[n(\#M)_{\text{surf}}]
\]

\[
\Delta_{\#M}^\phi S_{\text{M,298}}^{\text{surf}} - \Delta_{\#M}^\phi S_{\text{M,298}} = -R(\delta - 1)\ln \Gamma_{\#M}
\]

\([n(\#M)_{\text{surf}} \text{ is the total molarity of sites } \#\text{ at site density } \Gamma_{\#M} = \Gamma_{\#M}^{\text{surf}}\] depend on \(\delta\) and on the chosen value of \(\Gamma_{\#M}\) (1) or \(\Gamma_{\#M}\) (2). Upon adsorption of aqueous M, several H₂O molecules must be liberated from its solvation shell and from the MWI. Thus, a standard-state density \(\Gamma\) should lead to ‘standard’ \(\Delta_{\#M}^\phi S_{\text{M,298}}^{\text{surf}}\) and \(\Delta_{\#M}^\phi S_{\text{M,298}}\) effects consistent with known entropies and volumes of hydration of aqueous cations (cf. [5]). We find that \(\Gamma\) cannot be chosen arbitrarily; setting it close to the density of H₂O molecules in the surface monolayer (2·10⁻⁵ ± 1·10⁻⁵ mol·m⁻²) [6] leads to entropy and volume effects related to \(\times\) which are compatible with the available data on partial dehydration of aqueous ions and surfaces upon adsorption. In turn, this provides a constructive basis for future discussions aimed at reaching the ultimate thermodynamic convention on standard states of any-dentate surface complexes on MWIs.

Mantle volatiles in groundwaters near the San Andreas Fault

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Groundwater samples were collected from 19 wells along the San Andreas Fault (SAF) in the Cuyama, Cuddy, and Mil Potrero Valleys in southern California, USA. Previous work has shown leakage of mantle He via the SAF indicative of a focused mantle contribution to the surface. In this study, we assess the relation between He, a major volatile phase, and CO2, the hypothesized carrier of the helium from the mantle.

The isotopic composition and concentrations of dissolved gases were determined. Measured 3He/4He ratios were compared to the 3He/4He ratio of air = 1.4 x 10^-6 = Ra, to determine whether groundwaters were enriched in crustal (0.02Ra) or mantle (8Ra) helium. Concentrations of He, corrected for air-bubble entrainment, varied from 3.0 to 58.1 x 10^-8 cm3STP g-1H2O. 3He/4He ratios varied from 0.46 to 3.58 Ra, consistent with mantle He in all samples (up to ~50%). A subset of 10 samples were analyzed for CO2 and 13C; concentrations of CO2 varied from 0.059 to 0.223 cm3STP g-1H2O, and the 13C of the CO2 varied from -21.50 to -11.87‰. In groundwater, 13C ratios of ~-6‰, and elevated CO2 concentrations may indicate the presence of mantle volatiles, particularly when they co-occur with high 3He/4He ratios. Measured CO2/3He ratios varied from 64.1 to 1632 x 10^9 (mantle CO2/3He = ~1.5 x 10^6).

Samples were collected from Quaternary alluvium filled valleys formed by motion along the northwest-trending, right-lateral strike-slip SAF. The flux of deep mantle fluids to the seismogenic zone at high hydrostatic pressure may cause fault rupture, and transfer volatiles into the shallow crust. 3He/4He and 13C ratios, and He and CO2 concentrations are highest in the wells located in the Cuddy and Mil Potrero valleys, which are closest to the SAF. Samples with the highest 3He/4He ratios also had the lowest CO2/3He ratios. However, the eight wells sampled in the Cuddy and Mil Potrero valleys were located <1km from the SAF, yet their 3He/4He and CO2/He ratios varied by up to an order of magnitude suggesting heterogeneous fluxes of mantle volatiles along this 40 km section of the SAF.

Biological precipitation of calcite in stalagmites

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In recent years, speleothems have become an important archive for paleoclimate studies. To deduce paleoclimatic information from carbonate deposits, which is precipitated under non-equilibrium-conditions, it is important to improve the understanding of biological calcite precipitation.

In this study, laboratory experiments were conducted with calcium carbonate precipitating bacteria isolated from stalagmite deposits collected from Krem Syndai in Meghalaya, India. The medium used to culture these bacteria was designed in accordance to the drip water composition. We have isolated a new strain S4 that has been partially identified by 16S rDNA sequencing. The strain shows less than 95% similarity with any of the existing Bacillus strains involved in bio calcification. SEM and AFM studies are being carried out to understand the tomography of S4 strain.

Biocalcification rate of this strain was studied at regular intervals by studying the change in optical density, pH and calcite (wt%) precipitated in the medium. There is a positive correlation (r =0.925) between optical density and pH implying increased precipitation over the 40 day period. XRD was done to identify the minerals in the microbial precipitate. In addition the precipitate was analyzed for the isotopic composition of 13C and 18O.
Dry deposition: A major pathway of atmospheric dust particle deposition

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Acidic deposition is of major concern due to their detrimental effects including widespread acidification of soil, ponds, lakes, corrosion of building materials, injury to vegetation etc. The major mechanisms of removal of pollutants from the atmosphere to earth surface are dry deposition, wet deposition and occult deposition. Dry deposition is an important process for Indian climatic conditions as dry conditions prevail for most part of the year while rains are confined to short monsoon period. Direct measurements of dry deposition on natural surfaces are significant because measurements made so far are on surrogate surfaces that do not simulate the natural surfaces. Dry deposition flux was higher on rougher surface of Cassia leaf comparison to leaf of Ashok because it prevented the re-entrainment of deposited particles and therefore has higher deposition flux. Contribution of alkaline components is higher towards total dry deposition and hence dry deposition is basic in nature, which is dominated by the soil-derived elements Ca2+ and Mg2+. NH4+ also plays important role in neutralization. Three major sources responsible for dry deposition of major ions are combustions for F-, Cl-, NO3-, SO42- and K+, road dust/soil for Ca2+, Mg2+ and NH4+ and brick-kiln industries for Na+ and F-. The deposition velocities are relatively larger for cationic species than anionic species probably because the soil-derived aerosols (Na+, K+, Ca2+, and Mg2+) have higher MMDs.

Integrated GIS approach for characterisation of hydrogeochemical processes governing the groundwater quality in Sabarmati basin, Gujarat, India

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Factors influencing the groundwater hydrochemistry in pre and post monsoon season were evaluated for a part of Sabarmati river basin of Gujarat, a hub of intense growth of agricultural and industrial activities. Samples were collected on the basis of spectral signature of vegetation and soil as observed on satellite image. 14 water quality parameters were analysed which formed the attribute database for spatial variation of respective parameter using GIS. Graphical plots were used to decipher the hydrogeochemical process occurring in the study area. Gibbs plot, USSL diagram, % sodium and SAR were used to verify the suitability of groundwater for irrigation. It was observed that leaching of wastes disposed from anthropogenic activities and agrichemicals is the major factor along with the natural processes such as weathering, dissolution and ion-exchange. Control of indiscriminate and unplanned exploitation of groundwater, application of fertilizers and disposal of industrial wastes in the affected areas can possibly ensure groundwater protection from further pollution and depletion.
Porewater composition of cores from Palinuro sea mountain, Italy

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During RV Meteor cruise M73/2 (14-30 August 2007), cores were sampled from a submarine hydrothermal vent site at the Palinuro volcanic complex in the southeastern Tyrrhenian sea, Italy. Pore water samples were taken from the sediment cores using rhizon-samplers. Results from one of the cores are presented showing a distinct pattern for certain elements.

The redox potential changes from 100-200 mV in the upper one meter to strongly reducing conditions (-170 mV) at a depth of 280 cm. The pH has a minimum of 6.1 at a depth of 110 cm. While Fe and Mo show their highest concentrations in the upper parts of the profile, Mn increases with increasingly reducing conditions.

Si, B, Li, Cs, Rb, and As show the same behavior as Mn. While this is expected for As, it is quite surprising for all the other elements which are not redox-sensitive. Major cations and anions as well as electrical conductivity do not change significantly over depth. Arsenic speciation showed a predominance of arsenate and arsenite to a depth of 80 cm. At 90 and 110 cm, mono-(10%), di- (18%), and trithioarsenate (25%) were detected besides arsenate (34%) and arsenite (14%). At 110 cm, trithioarsenate was the predominant species with 64% of total As, followed by 28% dithioarsenate. The geochemical pattern is an indication for upwelling geothermal water and mixing with ocean water in the upper part where Fe and Mo is released from sediment under slightly oxidizing conditions.

Time-resolved emission of iodine from seaweed measured with a new on-line mass spectrometric technique

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Molecular iodine and iodocarbons are released by macroalgae and phytoplankton into the atmosphere. These volatile iodine-containing compounds are involved in the tropospheric ozone depletion and the marine new particle formation. Recent studies suggest that biogenic emissions of molecular iodine rather than iodocarbons are the dominant source of reactive iodine atoms in the marine boundary layer [1]. Especially during low tide, when the seaweed is exposed to atmospheric air, increased levels of I2 were detected at different measurement sites [2],[3]. In this work we present a new application of the time-of-flight aerosol mass spectrometer for the determination of I2 in real-time. ToF-AMS were developed for the measurement of non-refractory atmospheric aerosols with high sensitivity [4]. In order to use the high sensitivity of the ToF-AMS for I2 measurements, I2 has to be converted from the gas phase into the particle phase by α-CD/NH4Br particles inside a 0.5 L flow tube before entering the ToF-AMS. LOD of 300 ppt was achieved for 1 min time resolution and could be improved to 60 ppt for 30 min time resolution. Additionally this method was compared to a recent developed method that combines denuder sampling of I2 and GC-MS analysis. The newly developed ToF-AMS method was used to explore the time-resolved emission of I2 by various seaweed species from the eulittoral und sublittoral zone of Helgoland (North Sea, Germany). For our measurements entire seaweed species were removed from sea water, shaken free of excess water and introduced into a 4 L chamber made of glass to simulate low tide conditions. Additional stress was applied to the seaweed by flushing a continuous flow of ozonated (20-150 ppb) synthetic air through the chamber to investigate the influence of ozone on the emission of I2. Furthermore, volatile iodocarbons were quantified by TD-GC-MS and compared to I2 measurements.


Mineralogical Magazine www.minersoc.org
Dynamical correlations in transition metal compounds

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The standard methods of density functional theory describe the electronic structure of materials in terms of Slater determinants. While such description proved useful in many cases, in transition metal compounds it is often not sufficient. We use the dynamical mean-field theory (DMFT) [1] to study such systems and phenomena related to electronic correlations. The examples include the spin state transitions in MnO [2] and Fe$_3$O$_4$ [3], driven by pressure, and in LaCoO$_3$ [4], driven by temperature. We discuss the relationship of the spin transition to the metal-insulator transition and tendencies towards long-range ordering.

Figure 1: The orbital resolved Mn-d spectral density in MnO for various specific volumes. The results correspond to the temperature of 1160 K.

We will show how the local electronic correlation leads to emergence of non-fermionic degrees of freedom, such as the local magnetic moments, and how their fluctuations influence the material properties. The talk will focus on the qualitative differences between the DMFT description and static mean-field theories such as LDA or LDA+U.


Phyllosilicate dissolution kinetics: experimental observations and Kinetic Monte Carlo modeling

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We present our recent results in the study of phyllosilicate dissolution kinetics. The major problem in this field is the influence of the layered structure on dissolution mechanism and the difference in reactivity between edge and basal faces. We use an integrated approach including experiments and modelling to understand real crystallographic control of dissolution kinetics. Vertical Scanning Interferometry allows us to observe mineral surface topography during the dissolution process, measure dissolution rates and access their spatial and temporal variability. Detailed information about surface structure has also been obtained from AFM work. We simulate the dissolution of phyllosilicates using Kinetic Monte Carlo (KMC) approach. This stochastic method links elementary reactions taking place on the mineral surface with the topographic outcome of these processes. The KMC model has been parameterised using activation energies of elementary bond-hydrolysis reactions obtained from quantum mechanical calculations. As a result, we have reproduced experimentally-observed dissolution patterns in our KMC simulations (Fig.1). The combination of these techniques will help us to understand complex behaviour of crystalline systems in the dissolution process.

Figure 1: Left: AFM image of etch pit on muscovite {001} face 3x3 μm; Right: Etch pit (50 x 70 nm) obtained from KMC simulations with the enlarged area above showing arrangement of cations (Si/Al)
The influence of biofilms on fluid flow and contaminant transport in porous media

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Subsurface biofilm growth is a relatively novel and cost-effective method of bioremediation. Multiple injections of nutrients into the subsurface stimulate biofilm growth, forming a biobarrier. Biobarriers are known to reduce hydraulic conductivity, as well as immobilise metals in the matrix of the exopolymeric saccharides (EPS), produced by bacterial cells.

This research focuses on observing the influence of biofilm growth on transport in homogenous and heterogeneous column experiments under various nutrient conditions, as well as visualising and quantifying biomass of these biofilms in situ using x-ray micro computed tomography (μCT). This study will provide insight into materials and processes pertaining to groundwater vulnerability and assess the viability of biofilms to reduce the transport of aqueous metal contaminants.

Biofilms were grown under continuous flow conditions in glass columns. A Pseudomonas putida culture was injected into the columns for biofilm growth. A decrease in hydraulic conductivity, column outflow and fluid velocity through the duration of the flow experiments was observed, which signifies bioflocing took place in the columns. Biomass distribution was examined using extraction methods and protein/carbohydrate analysis. Additionally, syringe column experiments were carried out in order to observe and quantify microbially mediated mineral precipitation using μCT. In separate experiments Sporosarcina pasteurii, a ureolytic strain, was injected into the syringes to enable biofilm development and also CaCO3 precipitation. The distribution of biomass, mineral precipitates and fluid flow paths in these experiments were visualised using x-ray μCT. Preliminary μCT imaging illustrates that for microbial processes in porous media, both biofilm growth and CaCO3 precipitation as a result of ureolysis, can be visualised and quantified using CT techniques and software.

High-pressure single-crystal elasticity of MgSiO3 and (Mg,Fe)SiO3 perovskites at pressures of the Earth's lower mantle

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Sound wave velocities obtained in seismology are at the moment the only direct measure of the properties of the Earth's lower mantle. In order to use such measurements to constrain the chemical and thermal state of the Earth's interior, however, knowledge of the pressure dependence of acoustic wave velocities of model minerals is essential. MgSiO3 perovskite-type structures, with the end-member composition or containing some amount of Fe or Al, have been the subject of several studies, since are likely the primary lower mantle constituent. Experiments, however, are limited either to room pressure conditions [1, 2] or to aggregate materials [3, 4] due to the challenge of synthesizing and recovering high-quality single-crystals of this high-pressure mineral. Therefore the best knowledge of the full elastic constant tensor of orthorhombic (Mg, Fe)SiO3 perovskites results from first principle calculations [5, 6].

We succeeded to synthesize and select good quality single crystals of MgSiO3 perovskite (Mg - end member) and (Mg, Fe)SiO3 perovskite containing up to 4% of Fe. The crystals are prepared for high-pressure Brillouin measurements using FIB (focused ion beam) technology providing double side parallel cutting of the surfaces with required dimensions and quality.

We present the data of simultaneous measurements of sound velocities (by brillouin spectroscopy) and density (by single crystal x-ray diffraction) vs. pressure of the perovskite single crystals loaded in diamond Anvil cell with He pressure medium. Behavior of elastic constants calculated from these data and effect of Fe will be discussed in the presentation.

High magnitude MIF-S due to increased atmospheric $p(O_2)$

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Earth’s atmosphere experienced several profound changes in the geological past. Among these was the Great Oxidation Event (GOE) at ~2.4 Ga as indicated by the subsequent absence of mass independently fractionated sulphur isotopes (MIF-S). The temporal evolution in MIF-S from low towards high magnitude was recently suggested to reflect changes in the total atmospheric composition and not exclusively resulting from variations in $p(O_2)$. [1] proposed that a rise in the atmospheric SO$_2$/H$_2$S ratio enlarged the magnitude of MIF-S.

Black shales from the Superior craton (2.71 Ga) record a high magnitude MIF-S signal ($\Delta^{34}$S up to 4‰) following a period with greatly attenuated MIF-S between 3.2 and 2.7 Ga. Their $\Delta^{34}$S vs. $\Delta^{36}$S relationship shows a slope of -1, which appears to be a typical signature of rocks younger than 2.7 Ga. We interpret this shift towards high magnitude MIF-S and the concomitant change in the slope of $\Delta^{34}$S vs. $\Delta^{36}$S at 2.71 Ga as a consequence of a rise in atmospheric SO$_2$/H$_2$S. However, we suggest that a rise in atmospheric $O_2$ ultimately caused this increase, not variations in volcanic outgassing [1]. An increase in atmospheric $p(O_2)$ would have strengthened the conversion of H$_2$S to SO$_2$ resulting in a higher SO$_2$/H$_2$S ratio. Such a scenario would be consistent with a proposed onset of oxidative weathering already at 2.7 Ga [2]. Still, a generally reducing atmosphere kept oxygen levels below 10$^{-5}$ PAL, low enough to allow for MIF-S until the GOE at ~2.4 Ga.


Internal structure of icy satellites of Jupiter and Saturn and subsurface oceans

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Models of the internal structure of icy satellites have been constructed on the basis of the mass and moment of inertia constraints, geochemical constraints on composition of silicate fractions of ordinary and carbonaceous chondrites, and thermodynamic data on the equations of state of minerals and high-pressure ices [1, 2]. The mass and moment of inertia values are used as input data for determination of the thickness of an outer water-ice shell, the density distribution with depth, and the core sizes and masses. The equilibrium phase assemblages in the system Na$_2$O-TiO$_2$-CaO-FeO-MgO-Al$_2$O$_3$-$SiO_2$ were calculated using the technique of free energy minimization combined with the Mie-Grüneisen equation of state. The density variations in the mantle and Fe-S core radii are found by the Monte-Carlo method. The allowed thickness of Europa’s H$_2$O layer (whether liquid or ice) ranges from 115 to 135 km (6-8% of total mass) for a L/LL-type chondritic mantle [2]. Two alternative models of Ganymede’s outer shell composed of the high-pressure ice phases or of water and ice are considered. The thickness of the shell is in the range 800-900 km. The content of H$_2$O in Ganymede’s outer shell is 46-48% [1]. We show that Callisto must only be partially differentiated into an outer ice-I layer, a water ocean, a rock-ice mantle, and a rock-iron core. The maximum thickness of the outer water-ice shell is up to ~300 km and that of the internal ocean is about 150 km. The total amount of H$_2$O in Callisto is found to be 48-55 wt%. The results of modelling support the hypothesis that Callisto may have an internal liquid-water ocean [2, 3]. The correspondence between the density and moment of inertia values for the Galilean satellites shows that their bulk compositions may be, in general, similar and may be described by the composition close to a material of the L/LL type chondrites [1-3]. Planetesimals composed of these types of ordinary chondrites could be considered as analogues of building material for the rock-iron cores of the Galilean satellites. A comparison of the internal structure of Ganymede and Callisto with that of Titan has been made.

Geochemical and isotopic analyses of non-volcanogenic hot springs in central Japan

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The main aim of this study is to contribute to better understanding of fluid processes occurring in subduction zones with a comprehensive framework involving slab-derived fluids to near-surface fluids such as seawater, meteoric water and hot spring waters.

Our previous geochemical research on the Arima-type brine, anomalous non-volcanogenic hot springs with extreme high 3He/4He (e.g. [1, 2, 3]), identified and characterized the concentrated source brine in a robust multi-elemental/isotopic space, and so far, supports the idea that NaCl-CO2-rich aqueous fluids, which are possibly slab-derived fluids originated from subducting oceanic crusts, might have uprisen from a deep part of the forearc region and might supply solutes, gases and water itself to the brine.

While several other studies estimated the contribution of slab-derived fluids to island-arc magmatism (e.g. [4]), in non-volcanic or forearc regions, their involvements have been hardly found.

Therefore we extended our research area from the Kinki district in southwest Japan to forearc regions in central Japan, where two different slabs have been subducting, which might imply that one could expect involvement of two different slab-derived fluids. Along the Median Tectonic Line, which divides the adjacent forearc region in two, there are several non-volcanogenic hot springs, some of which are thought to be classified as the Arima-type brine. Here we present the results of our geochemical and isotopic analyses of these hot springs in forearc regions in central Japan.


Structure and compositions of zircon grains from lower unites of Norilsk lava section

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We intend to perform high precision absolute dating of lower unites of Norilsk volcanic section in order to understand evolution of Siberian flood basalts and their relation to P-T mass extinction [1]. For that purpose we picked up zircon grains from lower unites of Norilsk volcanic suit: Ivakinskaya (Iv), Severminskaya (Sv), Gudchikhinskaya (Gd) and Tuklonskaya (Tk) units. Here we report the first data on the structure and composition of 275 zircons grains obtained by CL, EPMA and LA ICP-MS techniques.

The studied zircons were subdivided into three groups. The group 1 (almost 70% of studied grains) includes euhedral grains with thin oscillatory zoning, group 2 (25% of population) consists of euhedral grains with low fluorescent cores surrounded by oscillatory zoned rims, and group 3 (5% of population) contains almost unzoned rounded low fluorescent grains. The groups 1 and 2 show week compositional zoning with slight decreasing of REE concentration towards the rim. They include the following minerals shown in the order of decreasing frequency: apatite, sphene, feldspars, crystalized melt, ilmenite and quartz. They possess relatively high Th/U ratios (0.3-2), are enriched in HREE and are likely of metamorphic origin.

We conclude that zircons of group 1 and 2 were likely crystallized in situ in basaltic flows and are good candidates for absolute dating.

Weakening and pore water evolution in the foreland of retreating glacier, SW Spitsbergen

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Chemical weathering and soil forming processes which are associated with retreating glaciers contribute to high chemical denudation observed in polar regions. Retreating glaciers uncover fresh regolith, initial evolution of which may be dominated by few simple processes. The area of this study is the foreland of Werenskiold glacier near SW coast of Spitsbergen. This glacier has been continuously retreating during the last century by several meters a year [1]. The objective of this study is correlation between the chemistry of pore waters and the mechanisms of alternation or dissolution of minerals present in regolith with respect to the distance from the glacier front (age of exposure). This is a part of large research effort on weathering, soil formation and initial microbiological activity on a foreland of Arctic glacier initiated with the International Polar Year in 2007.

Werenskiold glacier basin is eroded in metamorphic rocks which belong to Precambrian Hecla Hoek Succession. These are mostly carbonates, quartzites, phyllites, shists, greenshists and amphibolites [2]. In accordance with other studies, the carbonate dissolution dominates in the youngest glacial sediments while silicate weathering is relatively significant in the oldest sediments. The composition of water can be explained mostly by dissolution/crystallization accompanied with redox reactions. Alterations of minerals identified with optical microscopy, XRD and SEM-EDS include dissolution of carbonates and oxidation of pyrite accompanied with formation of clays. Systematic changes between water samples correlate with distance from the glacier front (with the age of soils): e.g. the pH decreases from 8, 6 to 7, 7 while TDS increases from 133 to 748 mg/L. Inverse modeling with PHREEQC was used to propose the mechanisms of mineral transformation. The waters evolve from carbonate-dominated to sulfate-dominated. This might indicate that with time, pore waters reach the equilibrium with carbonate minerals while being countinuously supplied with SO₄²⁻ from sulfides oxidation.

The research is supported by MNiSW grant N N307 473638.


Roles of sulfate and Fe³⁺ reduction on microbial community development

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To better understand the roles of sulfate- and/or iron-reduction on microbial community development, bicarbonate-buffered batch systems were created with acetate or lactate as the electron donor. Added electron acceptors included 2-line ferrihydrite, goethite, or lepidocrocite, in the presence or absence of sulfate. The batch systems were inoculated with the native microbial community present in a subsurface sediment. The rate of Fe³⁺ reduction was low in the absence of sulfate. However, the rate and extent of Fe³⁺ reduction increased more than 10 times with 10 mM sulfate. Sulfate reduction occurred concurrently with Fe³⁺ reduction suggesting abiotic Fe³⁺ reduction by sulfide. X-ray absorption fine-structure (XAFS) analysis confirmed the formation of ferrous sulfide as the major secondary mineral phase in these incubations. The rates of sulfate and Fe³⁺ reduction were significantly faster with lactate than with acetate. Lactate promoted both sulfate and Fe³⁺ reduction in all incubations, while acetate stimulated sulfate and Fe³⁺ reduction only in ferrihydrite and goethite incubations. Acetate oxidation was coupled with sulfate and Fe³⁺ reduction; however, lactate was rapidly fermented to acetate and propionate, followed by propionate oxidation coupled with sulfate reduction. Terminal Restriction Fragment Length Polymorphism (T-RFLP) yielded unique microbial community profiles. The presence of sulfate resulted in distinct community development likely due to the proliferation of acetate- or propionate-utilizing, sulfate-reducing bacteria. During the experiment, the community in lepidocrocite incubations evolved in a very different way compared to those in the other Fe³⁺ (hydr)oxide incubations indicating that the nature of the Fe³⁺ (hydr)oxide can affect microbial community development. However, after the complete consumption of sulfate the microbial community compositions in all incubations (except lepidocrocite plus acetate incubation) were similar to each other. These results show that the availability of sulfate, the type of Fe³⁺ (hydr)oxide present, and the added electron donor can have a strong effect on the development of subsurface microbial communities.
Deciphering the evolution of continental crust: Insights through Laser Ablation Split-Stream (LASS) petrochronology

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One of the biggest challenges in the determination of the timing and rates of continental subduction is tying the age of a particular mineral to the conditions (i.e. pressure, temperature, fluid composition) at which that phase grew. Recent advances in microbeam techniques have greatly increased our understanding of crustal evolution by enabling this linkage. The most common target for U-Th-Pb petrochronology is zircon: its REE pattern reveals the coexistence of garnet (depleted HREE) and plagioclase (positive Eu/Eu*) and cathodoluminescence imaging can be used to link the ages and trace-element concentrations of spot analyses. The age of monazite can also be linked to certain conditions: most commonly, yttrium zoning is used as a proxy for growth in the presence or absence of garnet.

Here we present a more accurate, comprehensive, and simplified procedure to obtain petrochronologic data and thus assess the P-T-t conditions of any individual spot analysis. The LASS—laser ablation split-stream—technique consists of concurrent analyses of single laser ablation spots on both a multi-collector (U-Th-Pb age) and single-collector (trace-element data) ICP-MS. LASS allows both rapid (<1 minute/spot analysis) and high-precision (<1%/age population) measurements and an unambiguous link between mineral age and (re)crystallization conditions.

The Western Gneiss Region of western Norway provides the perfect natural laboratory to exemplify the advantages of LASS petrochronology. Zircons from a garnet-bearing gneiss show >20 Myr of (re)crystallization, however, REE data show that these zircons grew under three distinct conditions: 1) garnet-poor prograde growth at 425.8 ± 4.6 Ma, 2) garnet-rich peak growth at 406.9 ± 5.7 Ma, and 3) garnet-breakdown retrograde growth at ~400 Ma. Without LASS, making this distinction would be nearly impossible. Monazite can also reveal complex age/element zoning; monazite avoided from a meta-pelite yield high-Nd cores of 413.6 ± 3.9 Ma, Low-Nd mantles of 401.1 ± 4.4 Ma, and high-Y, low-Sr rims of 393.5 ± 3.4 Ma.

REE mineralization of high grade REE-Ba-Sr and REE-Mo deposits in Mongolia and China

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The exact causes and mechanisms responsible for the uniquely high levels of REE in carbonatites relative to any other igneous rock remain debated. To investigate these mechanisms, a large suite of REE-bearing carbonatites from Mongolia (Mushgai Khudag, Lugiin Gol, Omnot Oljii, Khurimt Khad Tolgod) and China (Daluxiang, Maoniuping, Huanglongpu, Huayangchuan, Bayan Obo) was examined. All carbonatites are predominantly composed of medium-to coarse-grained calcite (60-90%). Accessory non-carbonate phases include mainly apatite, alkali feldspars, fluorite, phlogopite, sulphates and sulphides. The principal REE hosts are fluorocarbonates (<20 vol. %) and monazite (<5 vol. %). Fluorocarbonates occur as complex intergrowths of bastnäsite with parasite or synchysite. Bastnäsite-(Ce), synchysite-(Ce) and monazite-(Ce) also rarely occur as discrete crystals. There is a structurally controlled compositional variation among the major REE minerals, but carbonatites from different deposits feature almost identical REE-HFSE mineralization patterns.

Chondrite-normalized whole-rock REE profiles exhibit a steep negative slope and lack detectable anomalies. The REE minerals show consistent enrichment in light REE (La/Sm)n=1.0–3.4. In this respect, the carbonatite-hosted REE mineralization differs from that in the world’s largest REE deposit at Bayan Obo, where the (La/Sm)n ratios are more variable and generally lower. The REE distribution patterns of individual REE minerals are similar, with the exception of Huanglongpu and Huayangchuan, where REE mineralization is associated with Mo and Mo-Th mineralization. At these two localities, whole-rock and mineral-specific REE patterns are broadly similar, but the latter show some enrichment in heavy REE.

We propose a similar mineralogical model for all investigated deposits with the exception of Bayan Obo. The high-grade carbonate-hosted REE deposits at Daluxiang and Maoniuping are nearly exhausted, but the little-explored Huanglongpu-Huayangchuan cluster has a definite potential as a viable REE resource of the future. Small- to medium-sized deposits in southern Mongolia may also have some economic value owing to their overall high grade (7-15 wt. % REE2O3) and a healthy global REE market.