Unravelling P-T-t paths: Pseudo-sections versus classical phase petrology

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Crystalline rocks record critical information about the magnitude and rates of geodynamic processes. Important factors such as: how deep; how hot; how fast; and for how long are all in some way encoded in the mineral assemblages, mineral compositions and microstructures. Our ability to estimate metamorphic pressure–temperature (P-T) conditions has improved markedly with the increased availability of thermodynamic data for both simple and complex solid-solution phases, internally-consistent thermodynamic datasets and powerful computer programs to manipulate this data for a variety of equilibrium calculations. An increasingly popular tool is the single composition P-T section (commonly termed pseudosection) which allows rapid determination of mineral assemblages, compositions and their modal amounts for a given bulk composition within a specified P-T window. Unfortunately, with the increasing popularity has come an increasing disregard for the fact that a rock in equilibrium can only define a single point on such a diagram and that P-T paths, interpreted due to compositional zoning, inclusion suites and reaction textures, cannot be reliably indicated on the same, single pseudosection. Fortunately, the solution to this dilemma already exists. It is possible to model the consequences of bulk compositional fractionation along a P-T-path and even to define local bulk chemical sub-domains (e.g. for a single inclusion or between two specific grains). Conventional geothermobarometry, typically utilising standardised formulations of exchange, net transfer or solvus reactions, is only of limited, indicative use. However, if one is confident of having identified a preserved equilibrium assemblage, and assuming that the compositions of the phases have not been subsequently modified, the same conventional thermobarometric reactions can be determined with thorough consideration of the P- and T- dependence of thermodynamic parameters, including activities, with the internally consistent data. Rocks in perfect (metastable) equilibrium are ideal for studying by a single pseudosection but of zero use for data. Rocks in perfect (metastable) equilibrium are ideal for parameters, including activities, with the internally consistent consideration of the P-T-thermobarometric reactions can be determined with thorough

Mercury distribution and speciation in a seasonal wetland impacted by mine waste

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Ephemeral pond waters and surface sediments were studied in a seasonal wetland adjacent to the former Sulphur Bank Mercury Mine and Clear Lake (CA, USA) in order to evaluate in situ stabilization treatments as a remedial option for Hg-contaminated sediments. Surface ponds fed during winter by acidic groundwater seepage from a pit lake on the adjacent mine site have high and variable total dissolved Hg concentrations ([Hg] = 70-2300 ng l⁻¹), but low methylmercury (Me-Hg) (<0.1% of [Hg]tot). Higher dissolved Me-Hg concentrations, comprising 22-41% of total Hg, are correlated with pond waters influenced by groundwater flux from Clear Lake with circum-neutral pH (~6.6-8.6) and relatively high dissolved organic carbon (~30 mg l⁻¹). Characterization by X-ray diffraction and X-ray absorption spectroscopy (XAS) showed sulfate-rich (gypsum, jarosite) and clay alteration phases in surface sediments influenced by acidic groundwater, and less altered primary minerals and the presence of calcite in neutral pH sediments. Results from bulk and micro-focused Hg XAS of sediments indicated the presence of metacinnabar (HgS (s)), most likely as residual mine waste particles, nearest the former mine with high sediment [Hg]tot concentrations (100-500 mg kg⁻¹). Sediments from weakly acidic and neutral pH ponds had lower [Hg]tot (3-15 mg kg⁻¹), but a higher fraction of Hg associated with extractable organic matter. There was no evidence in sediment Fe or S XANES spectra for the presence of reduced Fe-sulfide minerals, and all surface pond waters were oxidized, with measureable dissolved oxygen and low dissolved Fe. The lack of evidence for active sulfate or Fe reduction in neutral pH ponds with high dissolved Me-Hg suggests that Hg methylation is occurring in the subsurface, with possible transport of Me-Hg by organic matter complexation. Thus, remediation strategies must consider both (1) stabilization of residual HgS (s) particles, but limiting bacterial sulfate reduction and Hg methylation as pond water pH increases with remediation of the pit lake, and (2) transport of Me-Hg in groundwater to surface biological receptors where Hg bioaccumulation may occur.
Effects of microbial activity and electron shuttles on the reduction of U(VI) under sulfidogenic conditions

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Introduction
Recent studies suggest that electron shuttles such as low molecular mass quinones and humic substances may play a role in many redox reactions involved in contaminant transformations and the biogeochemical cycling of redox active elements. This study investigates the effects of 9, 10-anthraquinone-2, 6-disulfonate (AQDS), a synthetic electron shuttle often used as a surrogate for quinone moieties in humic substances, on transformations of Fe, S, and U under reducing conditions.

Experimental Methodology
Experiments were conducted in defined mineral medium containing 30 mM Fe (III), 5 mM sulfate, and 10 mM acetate, with and without 100 µM AQDS and inoculated with sediment from the Rifle, CO, USA, Integrated Field Research Challenge (IFRC) Site. After the system reached steady state with respect to Fe (III) and sulfate reduction, aliquots of suspension were collected from each system and one set was pasteurized at 70 °C for 1 hr. The suspensions were then spiked with 500 µM U (VI).

Discussion of Results
After 48 h, 100% of the added U was removed from solution in the non-pasteurized AQDS system. However, only 58%, 25%, and 11% of added U was removed in the no AQDS non-pasteurized, AQDS pasteurized, and no AQDS pasteurized systems, respectively. U XANES analysis of the hydrated solids indicated that, with the exception of the pasteurized system without AQDS, the majority (85-95%) of the U associated with the solids was reduced to U (IV). The results of the EXAFS analysis of U (IV) in the systems with and without AQDS (not pasteurized) are consistent with the formation of nanoparticulate uraninite. The results of this study suggest that microbial reduction was the dominant process contributing to the reduction of U (VI) over the timescale of this experiment and that the presence of AQDS enhanced both biotic and abiotic/microbially mediated U (VI) reduction.

Age and origin of the Nuvvuagittuq Greenstone Belt

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The Nuvvuagittuq belt is dominated by mafic and ultramafic rocks metamorphosed to at least upper amphibolite facies. Primary U-rich minerals that might provide reliable dates for rock formation have yet to be found in the dominant lithology called the Ujaraaluk unit. Metamorphic zircons, rutiles and monazites are, however, present in the unit locally and give variably discordant results with 207Pb/206Pb ages ranging from 2.8 Ga to 2.5 Ga. The younger ages overlap 2686±4 Ma zircon ages for intruding pegmatites and Sm-Nd ages for garnet formation in the Ujaraaluk rocks suggesting this era as the time of peak metamorphism and metasomatism in the Nuvvuagittuq belt, coeval with regional metamorphism of the Superior craton. 143Sm-144Nd data for Ujaraaluk whole rocks provides a statistically poor isochron of 3814±300 Ma, but when separated by compositional groups, this ‘isochron’ is seen to consist of a series of ~2.7 Ga slopes emanating from a baseline distribution older than 4 Ga. Metamorphism at 2.7 Ga will have less effect on the 144Sm-142Nd chronometer because of 146Sm extinction prior to ~4 Ga. Expansion of the 142Nd dataset for the Ujaraaluk rocks and associated ultramafic cumulates continues to show a good correlation between Sm/Nd and 142Nd/144Nd that corresponds to an age of 4.359±45 Ga. The dataset now includes samples with superchondritic Sm/Nd ratios that extends the correlation to values of 142Nd/144Nd slightly higher than the terrestrial standard with a total range in 142Nd of more than 24 ppm. The upper Sm/Nd end of this correlation is defined by rocks that are interpreted as cumulates to compositionally related extrusive rocks indicating that this crystal fractionation had to occur while 146Sm decay was active, i.e. well before 4 Ga. Intruding gabbros give 143Nd and 142Nd isochron ages overlapping within error at 4.16 Ga also supporting an Hadean age for the belt. Eoarchean tonalites surrounding the Nuvvuagittuq belt show a deficit in 144Nd compared to the terrestrial standard, but plot to the low Sm/Nd side of the Ujaraaluk isochron suggesting that they are remelts of this type of mafic basement. The Nuvvuagittuq belt thus preserves over 1.6 billion years of early Earth history including an expanse of mafic crust formed only ~200Ma after Earth formation.
The punctuated evolution of the Earth: Geodynamic constraints and model predictions

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The preserved Precambrian crustal record is strongly episodic, and observation that has been attributed to preservational effects or episodic crustal production. These age peaks are associated with juvenile crustal production, voluminous high-temperature volcanism, massive mantle depletion, widespread orogeny and mineralisation, large apparent polar wander velocity spikes, and subsequent paleointensity increases. The impact of these events impinged on the glaciation record, atmospheric and ocean chemistry, and on the rise of oxygen. Here we assess a variety of geodynamic models for Precambrian dynamics against the swath of observational constraints available. We find that episodic behaviour from non-linear slab-driven models - such as mantle avalanches or episodic subduction events - are best able to simultaneously satisfy the majority of geological constraints. In such models, rapid descent of subducted material into the mantle drives fast plate motions and convergence at the surface. This is accompanied by large-scale upwellings of deep hot mantle which contribute to voluminous volcanism. Currently, it is not possible to differentiate the ultimate cause of non-linear plate behaviour solely from the geological record, however, dynamic simulations under Earth-like conditions may be able to secrete.

Redox variable trace elements

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As a change in the oxidation state of an element is usually accompanied by a profound change in its geochemical properties, redox variable elements are potentially sensitive indicators of mantle differentiation processes. Prominent redox variable elements include V, Cr, Mo, the PGEs, Re and U, as well as the volatiles C, H, and S. While Fe is the most abundant redox variable element, likely amounts of Cr, C and S are enough to affect the complex interactions between oxygen content and oxygen chemical potential (or oxygen fugacity, fO2) that must be understood to quantify the redox state of a system. The presence of abundant Fe3+ and Fe2+ may obscure the redox state of a trace element in glasses quenched from natural silicate melts because electron exchange reactions (e.g. Cr2+ + Fe3+ = Cr3+ + Fe2+) can be too fast for the high temperature speciation to be preserved. Hence spectroscopic measurements on natural materials at room temperature may be misleading.

V occurs in three oxidation states under terrestrial mantle conditions, V3+, V4+ and V5+, with a huge variation in incompatibility, making this element a good monitor of mantle redox processes. Its properties may be utilized either through whole-rock abundances to deduce redox conditions during partial melting, or from phenocryst/matrix partitioning, to study magma crystallization. When applied to arc basalts, the two methods show disconcertingly disparate results, crystallization mostly being under oxidized conditions (long known from Fe3+/Fe2+ ratios), but from a source of similar redox character to MORB source. Mo systematics show promise for further investigation of this conundrum. U is of particular interest because of the importance of U-Th-Pb systematics in evaluating mantle evolution, and of U series disequilibria in understanding rate processes. While U4+ is slightly less incompatible than Th, U5+ and U6+ are much more incompatible. Significant fractions of U6+ are expected at natural fO2s, with U5+ making an unexpected but intriguing appearance at low pressures.
Petrogenesis of the oceanic crust from trace elements in basalt glasses

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Laser-ablation ICP-MS gives precise trace-element analyses on small areas of basaltic glasses, not only for the traditionally analysed trace elements (REE, HFSE, LILE and first-row transition elements), but also elements such as Be, Ga, Ge, As, Se, Ag, Cd, In, Sn, Sb, W, Ti and Bi. We have analysed >350 Ocean Floor Basaltic (OFB) glass samples from the Smithsonian collection [1] covering a global range in OFB from the Atlantic, Pacific and Indian oceans, for 53 trace elements, plus sulfur by electron microprobe. EMP analyses of the major elements are given in [1]. Principal Component Analysis of a set of 29 precisely determined (±2%) highly incompatible trace elements (HICE: here, all 26 Refractory Lithophile trace elements plus P, K and Pb) shows that 96% of their variance is contained in the first two PCs (93% with PCA on the correlation matrix). The further statistical treatment of this large data set uncovers a highly systematic variation of HICE with degree of low pressure evolution from beneath the variability due to source heterogeneity and melting processes. This cannot be explained by simple fractional crystallization but reflects magma eruption/discharge processes [2, 3], not evident from major elements, which are buffered along the olivine-plagioclase-clinopyroxene cotectic. This evolution systematically fractionates the HICE among themselves in a way that is not consistent with simple fractional crystallization, e.g. mean Th/U increases from 2.3 at 9.5% MgO to 3.3 at 5.5% MgO. Inverting the parental OFB composition allows average mantle source composition and degree of melting to be calculated independently of assumptions about ocean crust recycling. The result shows that OFBs are a product of a high degree of melting (20 to 25 %), from a source that is too depleted to be balanced by estimates of the composition of the continental crust. This seems to require a non-chondritic Earth [4].


Coupling, decoupling and metasomatism: A saga of crust-mantle relationships beneath NW Spitsbergen (Arctic Norway)

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Recent studies integrating mantle and lower crustal geochronology on xenolith samples, isotopic information from crustal zircons worldwide, and seismic tomographic imaging of deep lithosphere domains, suggest that over 70% of the present deep lithosphere formed by about 3 Ga. Subsequent tectonism has modified the lithospheric mantle and caused crustal reworking. The Bockfjord area of NW Spitsbergen (Norwegian Arctic) provides an ideal natural laboratory to track crust/mantle evolution and tectonism over >3.2 Ga. Quaternary alkali-basalt volcanism provides abundant xenoliths of mantle and crustal rocks from both sides of a major translithospheric N-S fault. Zircons from lower-crustal xenoliths (from both sides of the fault) have mainly Neoarchean/ Paleoproterozoic or Paleozoic U-Pb ages; several show ages and/or Hf model ages >3.2 Ga. Mantle-derived peridotite xenoliths east of the fault contain common metasomatic minerals rare in those west of the fault. Re-Os analysis of sulfides in xenoliths west of the fault show T_{RD} model ages to 3.3 Ga; major populations are 2.4–2.6 Ga, 1.6–1.8 Ga and 1.2–1.3 Ga, with rare Caledonian ages. However, sulfides in xenoliths east of the fault show maximum T_{RD} of 2.3 Ga with major peaks at 900–1100 and 400–500 Ma, identical to the spectrum of zircon ages of protoliths for exposed gneisses and schists east of the fault. These data demonstrate a major disjunct, on both sides of the B-B fault, between the Archean lower crust and a Proterozoic–Paleozoic upper crust; this suggests that the original Archean upper (and middle?) crust was detached from the lower crust and replaced by thrust sheets of younger material, probably during the major overthrusting of the Caledonian orogeny. The striking differences in the SCLM on either side of the B-B fault suggest major transcurrent movement, juxtaposing lithospheric sections that evolved discretely at some distance from one another. West of the B-B fault, the presence of Archean lower crust overlying Archean SCLM suggests coupling of the crust and mantle for ≥3 Ga.
In situ U-Pb dating of rutile in UHT granulites from the Gruf Complex, European Central Alps

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In situ U-Pb dating of rutile directly in thin sections preserves textural information including inclusion relationships. Grains included in some minerals such as garnet may preserve older U-Pb ages than matrix grains due to sluggish Pb diffusion through the host mineral and can provide additional constraints on P-T-t evolution.

The Gruf Complex of the Central Alps consists of amphibolite migmatitic gneisses and relict ultra high temperature (UHT) charnockite and sapphire-bearing granulites. Whether the UHT event occurred during the Permian Variscan orogeny or the Tertiary Alpine orogeny is a matter of debate [e.g. 1, 2, 3]. Amphibolite facies metamorphism and migmatization began at ~32 Ma in the Central Alps, and temperature may have remained >640 °C until 22 Ma [4, 5]. The Gruf Complex lies structurally below the Bergell pluton, which crystallized between 32 and 30 Ma [6], and was intruded by the Novate granite at 24 Ma [7].

Rutile in the Gruf granulites was analyzed using laser ablation inductively coupled mass spectrometry. Inclusions in garnet, orthopyroxene, biotite, and sapphire as well as grains in the matrix and leucosomes were dated to determine if included grains preserve older ages than matrix grains. Average \(^{206}\text{Pb}/^{238}\text{U}\) ages uncorrected for common Pb range included grains preserve older ages than matrix grains.

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Is mineral precipitation the reverse of dissolution?

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Mineral precipitation and dissolution are fundamental processes governing fluid-solid reactions in nature and chemical mass transfer in the crust; the accurate description of the rates of these reactions within geochemical modelling codes holds the promise to quantify in real time the fate and consequences of processes ranging from radioactive waste disposal and carbon storage to the formation of hydrothermal ore deposits. Based, on the principle of detailed balancing, it has commonly been assumed that mineral precipitation can be described as the reverse of dissolution; transition state theory rate expressions that successfully describe mineral dissolution as a function of degree of fluid saturation state have been adopted to predict corresponding precipitation rates.

Surface sensitive microscopy suggests similar mechanisms at near to equilibrium; both dissolution and precipitation adds or removes material to existing active sites resulting in a linear dependence of rates on chemical affinity. At far from equilibrium etch pits form on dissolving surfaces, and analogous nuclei form on precipitating surfaces. The differences between dissolution and precipitation, however, stem from the existence of grain edges, which are active sites for dissolution but not precipitation. Moreover, the removal of material from edge sites creates additional active sites for dissolution, but precipitation fills active sites. As a consequence, steady state precipitation is dominated by nucleation in contrast to dissolution which removes material from continuously renewed active sites. This conclusion is supported by our recent measurement of quartz and magnesite dissolution and precipitation rates [1, 2]. Precipitation on grains having pre-existing active sites is consistent with the reversibility of dissolution whereas precipitation on pristine crystals is inconsistent and following independent rate equations.

Si isotope fractionation during precipitation of silica by cyclic freezing and adsorption of monosilicic acid on gibbsite

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Cyclic freezing of aqueous solutions containing silicic acid can be used to precipitate amorphous silica through complex precipitation-dissolution reactions. In such a dynamic system kinetic isotope effects during an unidirectional transfer from silicic acid to a solid may be equalized by cyclic dissolution of the previous precipitated silica and slow isotopic equilibrium between solutions and solids is potentially attained.

We performed several sets of freeze-thawing experiments to decipher the silicon isotope fractionation during precipitation of amorphous silica at pH 4.5 and 7. The initial solutions contain 1.6 mmol L⁻¹ of Si and 0.1 or 1 mmol L⁻¹ of Al (TEOS and Al(NO₃)₉H₂O). The solutions were frozen and thawed within 24 hours by up to 130 cycles and sampled at regular intervals.

Experiments with high initial Al concentration ([Al] = 1 mmol L⁻¹) show changing ³⁰Si values with time. The ³⁰Si solution values increased during the first 20 freeze-thaw cycles to up to 2.4‰ and then showed a decline to almost starting values of 0‰ after 130 days. Experiments with low Al concentrations ([Al] = 0.1 mmol L⁻¹) remained at the value of the initial solution throughout.

Supplementary adsorption experiments, with monosilicic acid (0.36 mmol L⁻¹ Si) and gibbsite (55 m² L⁻¹) were carried out at pH 7. Adsorption of silicic acid results in an increase of ³⁰Si values and a quasi isotopic/chemical steady state is reached at ~ 300 h.

Our results indicate that upper crustal rocks of the Oman ophiolite (lavas and sheeted dikes) exhibit: (i) pervasive alteration due to intense circulation of seawater; and (ii) microbial reduction of seawater sulfate occurring within the lavas during low-temperature alteration. Samples from the gabbro/sheeted dike transition zone and lower crustal rocks are affected by a high-temperature alteration resulting in leaching and redistribution of sulfide-S. ³³S* values of Cr-reducible sulfur (CRS) between -0.020‰ and -0.038‰ clearly differ from those of upper crustal rocks (Fig. 1). This could either suggest that intense sulfur leaching processes operate in those units, or that oceanic lower crust has a primary multiple sulfur isotopic composition that deviates from the postulated mantle value (³³S* = 0.0‰; [1]). Samples from the mantle portion of the Oman ophiolite display the widest ranges in ³⁴S and ³³S* reflecting multi-stage serpentinization processes.


A profile of multiple Sulfur isotopes for the Oman ophiolite

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The Oman ophiolite is regarded to represent the best example of fast-spreading oceanic lithosphere on land. Here, we present the first multiple sulfur isotope profile through all components of the (ancient) oceanic lithosphere (Fig. 1), together with sulfur abundances and a petrographic study.

![Figure 1: Δ³³S* values of Cr-reducible sulfur versus depth for a composite section through the Oman ophiolite; Δ³³S* = δ³³S - 1000 x ((1 + δ³⁴S / 1000)⁰.⁵¹⁵ - 1); GSDTZ represents the gabbro/sheeted dike transition zone.](image-url)
Geochemical behavior of As originated from acidic thermal water during river transport and sedimentation mechanism

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We investigated change in the physico-chemical and redox status of As originated from the acidic Tamagawa thermal waters during transport in Shibukuro and Tama Rivers and sedimentation mechanism in the watershed.

The predominant dissolved As species in the thermal water was arsenite. However, this species was rapidly oxidized. Thus, the geochemical mobility of arsenate was mainly controlled by the sorption onto hydrous ferric oxides (HFO). Most HFO sorbing As was transported and effectively settled onto the downstream man-made lake.

Most of As in riverbed and shallow part of lake sediments were extracted as reducible phase, indicating that they are originated from the Tamagawa hot spring area transported as HFO sorbates. Furthermore, XANES spectra reveal that As existed as As (V). On the other hand, As in deep part of lake sediments could not be extracted by reducing agent and XANES spectra reveal the conversion to As (III). The arsenite and ferrous ion was also detected in the interstitial water. These results indicate that HFO sorbing As was reduced during the sedimentation process.

The iron-oxidizing bacteria inhabited in acidic river water. The inhabitations of several microorganism including sulfate-reducing bacteria in deep part of lake sediment were also confirmed. Taking these facts into consideration, the As mobility in this river system would be possibly controlled by the bacterial activities.

Development of the modern-style geochemical cycle of uranium by 3.5 Ga: A solution to the ‘lead paradox’

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From analyses of redox-sensitive elements in many paleosol-, shale-, and submarine basalt- sections 3.5-2.5 Ga in age, we have recognized: (1) depletions of S and C, and depletions/enrichments of U, Mo, Fe, Mn, Cr and Cu in the paleosols; (2) enrichments of U and Mo in many of the black shales; (3) enrichments of U, Fe III and Mo in the basalts that were affected by submarine alteration; and (4) Ce anomalies in many of the paleosols and submarine basalts. Therefore, the behaviours of redox-sensitive elements in these Archean rocks are essentially the same as those in Phanerozoic rocks. This suggests that the Archean oceans were poor in Fe, but rich in U and Mo, and that the modern-style geochemical cycles of redox-sensitive elements through the continental crust, oceans, oceanic crust, and mantle reservoirs have operated since at least ~3.5 Ga. The presence of highly radiogenic Pb in many Archean-age submarine basalts also supports this suggestion. The atmospheric pO2 >0.5 PAL is necessary to operate the modern-style geochemical cycle of U. Subduction of Fe III- and U-enriched oceanic crust may have created a large-scale heterogeneity of the mantle since ~3.5 Ga, including: (a) the Fe III/Fe II ratio, and (b) the ‘lead paradox’ where the Pb in the mantle, especially in the source regions of OIBs and MORBs, is more radiogenic than in the chondrite-modeled bulk Earth. Therefore, through the creation of the oxygenated oceans and atmosphere, microbes have influenced the geochemistry of the deep Earth and the nature of volcanism since ~3.5 Ga.
Trace element composition of size-fractionated particulates in the Mauritanian upwelling zone of the Eastern North Atlantic U.S. GEOTRACES section

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Sinking (>51µm) and suspended (<51µm) particulates were collected via in situ filtration during the first US GEOTRACES North Atlantic Zonal Transect on the R/V Knorr in October-November, 2010. Total and acetic-acid leachable compositional profiles for key trace elements and isotopes (TEIs—Fe, Al, Zn, Mn, Cd, Cu) and other TEIs of interest (Co, Ti, Ba, V, Ni, Mo) are presented from four stations along the eastern tropical North Atlantic oxygen minimum zone (OMZ) extending from the coast of Mauritania to the Cape Verde Islands.

This dataset provides the first look at full (16-point) ocean-depth profiles of size-fractionated particulate trace elements in this productive and biogeochemically complex region. Particulate inputs, including mineral dust deposition from the Sahara, resuspended particles from the African margin, and in bottom nepheloid layers, are examined via bulk compositional data. Acetic acid-leachable phases are used to examine scavenging and remineralization processes of redox-sensitive and surface-active TEIs, especially within the Mauritanian OMZ and along upwelling-driven transport pathways away from the African continent.

Information from these particulate analyses, and soon the full particulate section of the US GEOTRACES North Atlantic zonal transect, will provide critical insights into TEI remineralization length and depth scales, elemental scavenging behavior in the OMZ and benthic nepheloid zones, and trace nutrient recycling rates within and below the euphotic zone.

Isotopic fractionation of Mg, Ca and Sr in calcite and aragonite

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The alkaline earth metals such as magnesium, calcium and strontium play an important role in a variety of geochemical and biological processes. The element ratios (Mg/Ca and Sr/Ca) in marine carbonates have been used as proxies for reconstruction of the past environment. Recently several studies suggested that the study for the isotopic fractionation of the alkaline earth metals in marine carbonates has a potentially significant influence in geochemical research fields (e.g. Eisenhauer et al. 2009). However there are few studies for possible correlations between the level of isotopic fractionation of Ca and that of other alkaline earth metals during carbonate precipitation.

The purpose of this study is to see if there are any correlations between the isotope fractionation factor of Ca during carbonate precipitation and that of Mg and Sr. Moreover, we investigated whether fractionations of Mg, Ca and Sr isotopes could differ between calcium carbonate polymorphs (Calcite and Aragonite). In order to examine the isotope fractionation factor of Mg, Ca and Sr during carbonate precipitation, calcite and aragonite were synthesized from calcium bicarbonate solution in which the amount of magnesium was controlled based on Kitano method (Kitano, 1962). Calcium carbonates were also prepared from the mixture of calcium chloride and sodium hydrogen carbonate solutions for the purpose of comparison among the methods. The isotope fractionation factors were measured by MC-ICPMS (Nu plasma).

Results suggested that the level of isotopic fractionation of Mg during carbonate precipitation was correlated with that of Sr and that the change of the carbonate crystal structure could make differences of isotopic fractionations of Mg and Ca, however no difference was found in the case of Sr. In this presentation, the possible mechanism will be discussed.
Biotransformation Rare Earth Elements

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Geochemical behaviors of rare earth elements (REEs of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) are important to understand the migration of trivalent actinides fission genic REEs from nuclear power plants and high level radioactive waste. When REEs migrates in environments, their chemical states may change by the interaction with inorganic and organic materials. Many researchers have studied the interaction of REEs with inorganic materials. However, the biotransformation of REEs have not fully understood. We have conducted the research on the effects of microorganisms on chemical states change of REEs.

The REEs patterns of the distribution coefficients (K_d) for hyphae of Acremonium sp. showed no Ce anomaly. On the contrary, the REEs pattern of K_d for biogenic Mn oxides with Acremonium sp. showed positive Ce anomaly at pH 3.7 by oxidization of Ce (III) to Ce (IV) by Mn oxides. With increase of pH in solution positive Ce anomaly became smaller, and the polarity of Ce anomaly shifted from positive to negative around pH 6.5. This anomaly shift is probably caused by organic molecules released from the hyphae.

Presence of desferrioxamine B (DFO) showed negative anomaly of Ce in the REEs patterns of K_d for Pseudomonas fluorescens. Negative Ce anomaly came smaller with increasing contact time, caused by oxidaton states change of Ce (IV) in the Ce-DFO complex to Ce (III).

We found that Ce (III) phosphate nano minerals were formed on the cells surface of yeast Saccharomyces cerevisiae after exposure of Ce (III) solution with the resting cells, even though no phosphate is added. Ce (III) ions were first adsorbed by the functional groups of cells surface, followed by the chemical states change by the reaction with phosphate ions released from inside the yeast cells.

These findings indicate that microorganisms affect geochemical behavior of REEs.

Carbonate dissolution at oceanic atolls: A CO₂ sequestration option

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Carbon dioxide storage in the ocean will eventually bring about the dissolution of carbonate in the ocean floor. Ohsumi [1] suggested the purposeful in situ reaction of CO₂ with the ocean-floor carbonate as a storage option of captured CO₂. However, the carbonate dissolution method [2, 3] proposed and discussed technically and geochemically so far has put the focus on siting the reactor vessel on land near emission sources of CO₂. The ocean bottom covered with carbonate sediments may not be suitable in applying the carbonate-dissolution method, because of high implementation cost as revealed by the research and development effort of the deep-sea Mn nodule mining and also of the associated environmental impacts on the open ocean. If the partial pressure of CO₂ is raised up more above one atmosphere by selecting the site of the dissolution underground, the volume of water required for the reaction to proceed could be saved, the reaction being:

\[
\text{CO}_2(\text{g}) + \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{HCO}_3^-(\text{aq}).
\]

Large scale coral atolls found typically in the Pacific ocean give an appropriate example of the installation site of the reaction system. When several hundreds tonnes H₂O coexisting with one tonne CO₂ are to be reacted with the ambient carbonate rocks at depths of a few hundred meters inside the atoll, ca. 20% of the injected CO₂ would be transformed into bicarbonate, reaching to the equilibrium where the pH value is above 6 and the CO₂ partial pressure is below one atmosphere. The drainage waste water containing the residual CO₂ (aq) and the reaction products, i.e. calcium bicarbonate solution would be discharged directly to the deep ocean for further dilution of CO₂ (aq). The discharge operation offers an opportunity for the measurement of CO₂ inventory, and more importantly contributes avoidance of the long term possible erosion of the atoll and its consequent impacts to the island surface.

The presented storage concept of captured CO₂ is essentially the ocean storage by dissolution of carbonate minerals, but eliminates the large-scale surface reaction plant.

Natural analogue study on long-term reaction of bentonite and highly alkaline groundwater

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Geological disposal of high-level nuclear waste has been planned and developed in many countries worldwide. In Japan, it is to be vitrified and an overpack enclosing metallic containers that contain the vitrified waste is to be placed in a deep geological repository with the multibarrier system consisting of an engineered barrier and a natural barrier by geological formations. One of the possible buffer materials for the engineered barrier is bentonite, which should possess the property of long-term stability, although the functions required for it depend on the method of disposal of the waste. When used with cement materials as reinforcing agents, however, the functions required for the bentonite-based barrier material may deteriorate due to such phenomena as dissolution and change of properties by highly alkaline groundwater formed by reactions of the cement materials with groundwater. Since it takes hundreds of thousands of years for the radioactivity of high-level nuclear waste to decrease to the natural background level, it is impossible to clarify the reaction mechanism of bentonite and highly alkaline groundwater in the laboratory for such a long time. An appropriate method to examine such a long-term system is natural analogue study that is an investigation of a natural system that has some similarities with a radioactive waste repository and its surrounding environment.

The Mangatarem district, in the Philippines, was chosen as a study area in this natural analogue study. Through the investigation of the Mangatarem district, we tried to elucidate the long-term interaction of bentonite with highly alkaline groundwater.

Analytical results reveal some differences between the trench and outcrop samples. Assuming that the source rock of bentonite and zeolite is common for the rock samples of the two sampling points, those differences are probably attributable to the difference in the reaction of the source rock with the highly alkaline groundwater that had come up along faults.

Iron isotopic signature for weathered ordinary chondrites: Application of the LAL sampling-ICP-MS technique for cosmochemical sample

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The laser ablation in liquid (LAL) is one of the most versatile techniques to produce the nanoparticles of the solid materials. Our recent research revealed the LAL can be also applied for the sampling technique of the solid samples to measure the elemental and isotopic composition using the mass spectrometer [1, 2]. The LAL sampling technique provides the micro scale sampling, sample integration, and the elimination of the coexistent elements through the ion exchange chromatography. These advantages enable the high-precision measurement of the micro region on the solid samples.

In this study, we have measured the $\delta^{56}$Fe and $\delta^{57}$Fe values of the Fe-Ni grains and the related weathering products in the ordinary chondrites. The cut pipette tip filled with deionized water was placed on the polished meteorite surface and the laser ablation was performed through the water layer. After the LAL procedure, the sample suspension was collected using the micropipette. The resulting sample suspension was decomposed and dissolved in conc. HCl, then the resulting solution was used for the $\delta^{56}$Fe and $\delta^{57}$Fe ratio measurements using the multiple collector-ICP-MS technique. The measured $\delta^{56}$Fe values of metal grains showed good agreement with the previously reported values [3]. In contrast, the iron isotopic signature for weathering products found in the identical meteorite samples revealed that the measured $\delta^{56}$Fe values were significantly higher than those for the inherent metal grains. It should be noted that the inherent part of the metallic grains were commonly surrounded by the weathered parts. Possible cause of the present large difference in the measured iron isotope ratios between the fresh and weathered metal grains will be discussed in this presentation.

Water and ethanol reactivity on chalk from water- and gas-saturated zones

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Adsorption and wettability properties of chalk in oil-reservoirs are highly affected by many factors. These factors include: the presence of inorganic, polymeric, and especially, organic additives on the surface.

To compare the behavior of samples with different levels of surface coatings, we analyzed the solid surfaces of chalk sampled from a water and a gas zone. We also examined how the adsorbed organic material affects the ability of chalk to interact with polar molecules such as water and ethanol. The changes in adsorption energy of water can be used to predict the changes in surface wettability, while ethanol adsorption studies can help in understanding adsorption mechanisms for polar organic compounds. For investigating porous solids such as chalk, vapour adsorption isotherm determination is an appropriate alternative technique to the methods usually used for adsorption studies.

Isosteric enthalpies of water and ethanol adsorption were examined on chalk samples before and after liquid (chloroform) – solid extraction of the organic matter and compared with the results for synthetic calcite. The chemical composition of the extracted organic fraction was established by chromato-mass-spectrometry and qualitative changes on chalk before and after the extraction procedure were monitored with X-ray photoelectron spectroscopy (XPS).

The XPS spectra show that extraction with chloroform leads to a relative increase in concentration of polar groups on the chalk surface. This is consistent with the extraction experiments, which show that the liquid extract from both chalk samples contains mainly nonpolar long-chain alkanes.

We observed a difference in water and ethanol adsorption behaviour caused by the nature of the solid and the adsorbate. Water adsorption depends on the presence of adsorbed polar groups and enthalpy of adsorption increases with decrease in amount of preadsorbed nonpolar organic matter, while ethanol adsorption is not influenced by amount of polar groups on the chalk surface. At the same time, ethanol bonds specifically to synthetic calcite with an energy of ~200 kJ/mol, which is 3-4 times higher than on chalk. The results can be used in interpreting the adsorption mechanisms for organic matter on natural oil reservoir materials and for modifying surface properties.

Low temperature alteration of serpentinized dunite; A case study from the Leka ophiolite complex

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Ecosystems based on water-rock interactions independent of photosynthesis have been known for the last decades. Systems where processes like serpentinization produce H2 and simple hydrocarbons supports the hypothesis of a H2 based subsurface biosphere. Such environments could be important analogues to systems where life originated. The low temperature water-rock interactions in ultramafic rock is poorly constrained. In this study we try to understand ongoing low-temperature reactions through textural, mineralogical and geochemical characterisation of a 50 m long rock core from the dunitic part of the Leka ophiolite complex, mid-Norway, in combination with geochemical analyses of groundwater emanating from this drill hole, and rainwater. Geochemical modelling has been used to describe ongoing processes in this system.

The core show different degrees of alteration from olivine-dominated, near unaltered dunite to nearly completely altered dunite consisting mainly of blocky serpentine with partly open veins lined with fibrous serpentine and brucite. Groundwater infiltration is thought to take mainly place in three major fracture zones in the most altered parts. Analysis of the groundwater show that the pH increases and the Mg and Si decrease as the groundwater evolves. The most evolved groundwater also has elevated levels of H2 and traces of CH4.

Since the main part of the water-rock reactions take place in the serpentine dominated part of the rock it is suggested that the H2 is a result of the reduction of ferrous iron from dissolving serpentine and brucite.
Experimental study of partition of rare elements between minerals and melts of diamond forming eclogite-carbonatite and peridotite-carbonatite systems

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The goal was to study interphase partitioning of trace elements in high-pressure melted eclogite-carbonatite \([\text{CPx}_{40-64}\text{Grt}_{16-40}(\text{SiO}_2)_{20}]_{59.3}\text{Carb}_{39.3}98.6\text{RE}1.4\) and peridotite-carbonatite \([\text{Ol}_{36-60}\text{OPx}_{16}\text{CPx}_{12-24}\text{Grt}_{12-24}]_{30}\text{Carb}_{70}99\text{RE}1\) systems doped with a set of trace elements: Li, Rb, Cs, Ba, Th, U, Ta, Nb, La, Ce, Pb, Pr, Sr, Nd, Zr, Hf, Sm, Eu, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, Sc, and Zn. Concentrations of trace elements in coexisting phases were determined using LAICPMS and the mineral-melt partitioning coefficients were calculated. The main feature of the trace element partitioning in high-pressure experiments is the different behaviour of light REE (La, Ce, Pr) in relation to medium and heavy REE (Nd, Zr, Hf, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, Sc, and Zn). Concentrations of trace elements in coexisting phases were determined using LAICPMS and the mineral-melt partitioning coefficients were calculated. The main feature of the trace element partitioning in high-pressure experiments is the different behaviour of light REE (La, Ce, Pr) in relation to medium and heavy REE (Nd, Zr, Hf, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu). Light REE are partitioned favourably into the melt phase, and the rest REE go into garnet, when the last is presenting. Comparison of the new experimental and published data for partitioning between garnet, clinopyroxene and carbonatite melt, as well as for garnet, clinopyroxene and silicate melt [1-4] shows a similarity in respect of trace element distribution of diamond-forming homogeneous carbonate-silicate melts studied and carbonatite or silicate melts equilibrated with the mantle silicate minerals.

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REE geochemistry, mineralogy and origin of manganese mineralization in the Derbent (Mahkeme Hill), Yozgat (Turkey)

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Artova ophiolite complex is located along the North western and east margin in Yozgat (Turkey). The Mn-deposits in the Derbent area is part of this ophiolite complex. This deposit banded and lenticular forms, is hosted by radiolarite and is generally overlying volcanics. Manyetite, manganite, pyrolusite and goethite are main constituents of the manganese ores in Mahkeme Hill (Derbent-Yozgat) area. The gang minerals in Derbent are quartz and calcite.

In chondrite normalized REE graphics samples are characterized by highly negative and positive Ce anomalies in area. Europium shows negative anomaly in all samples. The negative Ce anomaly is typical to submarine hydrothermal deposits and positive Ce anomaly is indicative of hydrogenous deposits [1]. The negative Eu anomaly shows contamination from the continental crust and/or sediment contribution via dehydration [2].


Figure 1: Chondrite normalized REE diagram for ore samples

Ce values in the Mahkeme Hill mineralization were computed and the anomalies were found as Ce<sub>anom</sub> < -0.1 in 9 samples and Ce<sub>anom</sub> > - 0.1 in 5 samples. These values are indicative of both oxic and anoxic sedimentation conditions. Chemically, the studied manganese deposit and associated radiolarite are very similar to these formed by hydrothermal – hydrogenous processes.


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Beyond petroleomics – Petroleum geochemistry for the 21st Century

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Petroleum geochemistry has been driven by analytical developments since the development of gas chromatography in the 1950’s and practical computerized GCMS technologies in the 1970’s heralding, in the 70’s and 80’s, the development of practical biomarker technologies and most of the source rock facies and maturity molecular concepts that we still use today. Recent advances in Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) technology now allow a more comprehensive analysis of polar constituents of fossil fuels. This new technology allows for the first time routine analysis of the broad range of complex polar compound mixtures that dominate source rock extracts and heavy oils.

In this study we will show the use of FTMS derived high molecular weight multi hetero component (HMWMH) complex compound class distributions to discriminate biodegraded oils from different source rocks from marine versus lacustrine systems and also differentiate oil charges from mixed facies marine source rocks. These new proxies are independent of microbial biodegradation alteration levels from Peters & Moldowan levels 0 to 8 (Peters and Moldowan, 1994) and show that it is likely that FTMS techniques and parameters may offer substantial advances over conventional GCMS based approaches to petroleum system characterisation. In addition, new insights into the compositional changes during in situ thermal recovery processes simulated in the lab under aquathermolysis and hydrotreating conditions will be shown.

The environmental impact of sewage effluent discharges in the Pracana River - Portugal

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The Pracana River is an important tributary of the Ocreza River. The Ocreza River is located in Central Portugal and has it source in an important Alpine chain called Gardunha. It starts at 1160 m altitude and stretches for 80 km until draining into the Tagus River. It has several creeks and tributaries along which there are several rural villages. The Pracana’s waters has an important role by being abundantly used in agriculture, the main economic activity of these communities, and for human consumption. Characterization, monitoring and control of the impact due to several wastewaters treatment plants discharges on water quality is of crucial importance.

This paper focuses on the Proença-a-Nova wastewaters treatment plant, which discharges directly into the Freixada River, a Pracana’s tributary. Twelve georeferenced water samples were collected between the sewage effluent discharge and the Pracana river confluence. Secondary inflows were identified and water samples collected downstream at approximately equal distances. The core of our study is the hydrological year of 2010. Sampling campaigns were conducted during three different periods: rainy winter (January), intermediate conditions (March) and dry season (June). The following chemical parameters were analyzed: biochemical oxygen demand (BOD), dissolved oxygen concentration (DO), dry residue, Ptot, Ntot, pH, temperature and microbiological parameters. The dissolved oxygen concentration (DO), biochemical oxygen demand (BOD) and the microbiological parameters were used as indicators for the presence of organic matter in the body of water, and as parameters for evaluating the environmental pollution.

The pollution simulation in the Pracana river was performed by a coupled hydrodynamic and water dispersion model. A water quality model was constructed applying to QUAL2kw software. The simulation results are consistent with field observations and demonstrate that the model has been correctly calibrated. The model is suitable for evaluating the environmental impact of wastewaters plant discharges on the Pracana River, allowing feasibility studies of different treatment schemes and the development of specific monitoring activities.
**U-Pb dating of very low-grade metamorphic titanite**

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Titanite is a common secondary mineral present in metabasites in the Chilean Andes. Its rather high closure temperature (<550°C) renders it very suitable for dating sub-to-low-grade metamorphism or hydrothermal alteration. In this study we tested the feasibility of dating very small grains of secondary titanite. Thirteen standard petrographic thin sections of Mesozoic volcanic rocks outcropping in the Main and Coastal cordilleras of central Chile (33-35°S) were selected for U-Pb dating by LA-MC-ICP-MS. The analyzed titanites occur as four different varieties: infilling amygdales or veins, within the groundmass, and replacing both former pyroxene and magnetite phenocrysts. The radiogenic Pb content is generally low and correlates with the type of titanite, i.e. the large titanites within amygdales (~200 µm) contain the most radiogenic Pb. The mean ages range from 48.5±6.5 to 147±22 Ma, with three distinct groups at 102-108 Ma, 80-85 Ma, and 49-62 Ma. One sample from the Coastal Cordillera yielded an age of 119.8±3.6 Ma (Fig. 1). The U-Pb ages do not correlate with either the amount of common Pb, or with the varietal type of titanite (Fig. 1). The U-Pb ages overlap with those previously obtained by K-Ar and Ar-Ar methods, which have been attributed to either very low-grade metamorphism, or approach the age of volcanism; however, several samples yield Cenozoic ages, which may represent a geologic event or related to secondary Pb loss.

**Low biodiversity tropics in a high CO2 median Mesozoic world**

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A strong latitudinal gradient in biodiversity, increasing to the tropics, is one of the most striking of modern ecological patterns. Late Triassic to Early Cretaceous tropical assemblages do not show this pattern, however. Most tropical and subtropical floral records from this time are characterized by low diversity and are overwhelmingly dominated by cheirolepidaceae conifers and their pollen, *Classopollis*. These conifers have been traditionally described as arid-adapted with features such as microphyllus leaves and thickened cuticle with sunken or papillate stomata. While some subtropical occurrences of cheirolepidaceae conifers are indeed associated with sedimentological evidence for aridity such as evaporites, many from the tropics are not and instead are found in settings incompatible with aridity. In contrast, the temporal distribution of these low-diversity assemblages tracks Mesozoic CO2, rising through the Triassic and falling through the Cretaceous as angiosperms become more prevalent. We suggest that these conifers were not so much arid-adapted, but rather specialized in extraordinarily hot, high-CO2 environments, regardless of precipitation.

The same pattern maintains at finer time scales. The end-Triassic extinction (ETE) exhibits a dramatic drop in biodiversity at pulsed ~3X increases in CO2 associated with Central Atlantic Magmatic Province (CAMP) basaltic eruptions. *Classopollis* massively increased in the tropics and subtropics as generic diversity of other pollen and spores dropped in direct association with the eruptions. However, perennial lake sediments and other indications of an enhanced hydrological cycle increased dramatically at the same time consistent with high CO2 and extremely hot temperatures, being the main drivers of cheirolepidaceae dominance and low biodiversity, not the lack of water.

High latitudes had dramatically higher diversity. At the ETE, these assemblages also suffered a huge drop in diversity among broader leaf forms consistent with thermal damage, but they never became as skewed as the tropics. Thus, relative to now, latitudinal diversity gradients were reversed at all temporal scales during times of very high CO2, plausibly because of near lethal temperatures.

![Figure 1: Titanite U-Pb ages.](image-url)
Incorporation of heavy metals into recent travertine formations at the Eyjafjallajökull volcano

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The release of heavy metals from water-volcanic rock-gas interaction and pristine volcanic ash-water interactions pose a serious environmental problem for water supplies. Thus it is interesting that the concentrations of waterborne pollutants monitored in the vicinity of active volcanoes are often much lower than predicted. Released heavy metals from the initial water-rock interactions are probably scavanged by and/or reincorporated into secondary precipitates including aluminium silicates, iron (hydr)oxides and carbonates. The purpose of this study was to investigate the capacity of naturally formed travertine to immobilise heavy metals.

Following the eruption of the Eyjafjallajökull Iceland volcano in the spring 2010, a new strong outlet of riverine CO₂ was observed via the river Hvanná, which indicates deep degassing into the water. A white mineral layer; at some places several cm thick, for hundreds of meters downstream was observed. The precipitation was identified solely as calcite with X-ray diffraction. Low concentrations of riverine Al and Fe provide a unique opportunity to examine the scavenging role of the precipitating carbonates exclusively. A gradual decrease of: conductivity from 1.8 to 1.1 mS/cm, alkalinity from 20.8 to 8.8 meq/kg, concentration of Ca, Mg, Cd, Cu, Mn, Sr, Ba and CO₂, and increase in the pH from 6.5 to 8.5, strongly correlated with the amount of precipitated travertine. Dissolution experiments show that bulk travertine incorporates the same metals. The water temperature was below 5 °C and an elevated atmospheric CO₂ partial pressure was detected near the river. The river water degassed downstream and pH increased, resulting in calcite supersaturation and precipitation. Our thermodynamic models suggest that, in addition to CaCO₃, Mg-, Sr- and Ba-carbonates and two phyllosilicate phases were supersaturated.

Our study provides valuable information for assessing environmental impacts for, e.g. volcanic eruptions or carbon capture and storage (CCS) projects in basaltic rock, such as the Icelandic multi-collaborator project ‘Carbfix’.

Enzymatic and abiotic hydrolysis of glucose phosphate adsorbed on goethite

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Organophosphates constitute a substantial part of the total phosphorus in soil. However, hydrolysis of the phosphate ester bond may be required in order to produce bioavailable phosphate. Adsorption on mineral surfaces can facilitate abiotic hydrolysis, but has also been suggested to block enzymatic hydrolysis. In this study we have investigated the enzymatic and abiotic hydrolysis of glucose-1-phosphate and glucose-6-phosphate adsorbed at the water-goethite interface. Sugar monoesters such as these have been indicated to occur at significant concentrations in soils.

To study the kinetics and molecular mechanisms of the abiotic and enzymatic hydrolysis we have used wet-chemical and spectroscopic techniques. Ion chromatography was used to obtain quantitative data, while a setup for simultaneous infrared and potentiometric titrations was used to investigate in situ the goethite-water interface reactions. We found that glucose phosphate forms three surface complexes on goethite in the pH range 3 – 10 differing in protonation states and hydrogen bonding interactions with neighboring surface groups. Below pH 7 the glucose-1-phosphate complexes are stable with respect to hydrolysis whereas at higher pH values a small extent of hydrolysis is detected. With glucose-6-phosphate the trend is reversed, i.e. hydrolysis occurs at low pH values. When an enzyme (acid phosphatase) is added the hydrolysis increases considerably. This increase coincides with adsorption of enzyme, and all experimental data indicate that the enzymatic hydrolysis is a strictly interfacial process. Furthermore, the enzymatic hydrolysis is strongly dependent on the amount of glucose phosphate adsorbed since the properties of the surface affect the enzyme’s mode of adsorption and hence it’s activity.
A study on the beach sediments of The Gulf of Fethiye (SW Turkey), focus on geochemical data

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This study is carried out to investigate sedimentary transport and depositional processes, heavy mineral distribution and possible economically important placer potentials of coastal beaches of the Fethiye Gulf. Investigation also forms part of a Project supported by the Ankara University Scientific Research Projects Office. To perform this, in September 2009, a large number of sediment samples were collected along the shoreline (A) and backshore (B) parts of coastal beaches of Fethiye and subjected to well-known sedimentary petrographic methods.

Figure 1: The distribution of Co, Cr and Ni concentrations in the beach sediments of Fethiye.

According to multielement analysis of sediments, Ni (657 ppm), Co (35, 5 ppm) and Cr (1605 ppm) contents are found to be higher than average values of Earth’s crust and sandstones values. Earth’s crust averages (ppm) for Co 25, Cr 100 and Ni are also given for comparison [1]. High concentrations of the elements can be related to the occurrences of ophiolites and bearing chromites on the coastal hinterland of the Fethiye Gulf. The total heavy mineral contents of the sediments showed parallel trend with an some element contents.


Experimental tests for the origin of Archean sulfur mass-independent fractionation during SO2 photolysis

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The signatures of Archean sulfur isotope mass-independent fractionation (S-MIF) provide critical constraints on the redox evolution of the early Earth’s atmosphere. Although S-MIF is likely to be sourced from SO2 photolysis, the physical origin of this unique isotope effect is yet to be identified. Recent studies suggest 1) selfshielding [1] or 2) isotopologue specific photoexcitation [2, 3] as the origin of observed S-MIF signatures. These two models imply the pattern of S-MIF is sensitive to the UV spectrum, and thus, the atmospheric components that absorb UV region between 190 to 220 nm, potentially providing significant new constraints on the chemical compositions of early atmosphere.

A series of laboratory experiments are in progress to test above two hypotheses during UV photolysis of SO2 (3SO2 + hν → 2SO3 + S). A flow-though photochemical reactor is used to examine S-MIF as a function of SO2 mixing ratio. Two broad band light souces (D and Xe arc lamp), with or without 200 nm bandpass filter, are used to test the effect of light spectrum. Detailed photohemial model using available rate constants suggests that S is formed by SO bimolecular collision (SO+SO → SO2 + S), and the photolysis of SO (SO+ hν → S + O) is a minor channel.

Experiments with D and Xe lamp produced similar MIF patterns (δ34S/δ32S and Δ34S/Δ32S ratios), suggesting S-MIF is not sensitive to the detailed shape of the UV spectrum. Although large δ34S isotope effect is consistent with [2], their cross section predicts the opposite signs of Δ34S for D and Xe lamp experiments. This suggests that the photoexcitation step itself may contribute relatively little to S-MIF. Instead, S-MIF may be originating from the isotope-sensitive quantum yield, such as curve crossing among various excited states SO2. We will also report the results from a newly constructed dual-flow cell system designed to test the SO2 selfshielding model at optically thin conditions.

The role of hydroxyl group (OH) in forming minerals

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There was studied the changes of the pyrrhotites structure when hydroxyl group (OH) is introduced into it. After synthesis (1273 °C) the samples were maintained at the room temperature (~ 25 °C) for 29 years in atmospheric conditions. The X-ray and chemical analysis analysis of the samples, which were maintained, showed that there are compounds containing hydroxyl group (OH) in the crystal structure. The samples contained parabutlerite, goethite, szomolnokite, rozenite, rhomboclase, pyrite and pyrrhotite.

For example the influence of hydroxyl group (OH) on the content of the formed szomolnokite was considered on the basis of calculating the thermodynamic potentials using the Bose-Einstein statistics. The theoretical calculations were compared with X-ray phase analysis data (table 1).

<table>
<thead>
<tr>
<th>S/Fe ratio</th>
<th>Percentage hydroxyl group (OH)</th>
<th>X-ray calculated</th>
<th>As calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.710</td>
<td>4.25</td>
<td>21.21</td>
<td>16.779</td>
</tr>
<tr>
<td>1.684</td>
<td>2.72</td>
<td>12.92</td>
<td>18.533</td>
</tr>
<tr>
<td>1.670</td>
<td>4.42</td>
<td>23.70</td>
<td>19.553</td>
</tr>
<tr>
<td>1.660</td>
<td>2.38</td>
<td>11.65</td>
<td>20.315</td>
</tr>
<tr>
<td>1.580</td>
<td>5.11</td>
<td>25.61</td>
<td>27.586</td>
</tr>
<tr>
<td>1.571</td>
<td>5.27</td>
<td>17.36</td>
<td>28.552</td>
</tr>
<tr>
<td>1.497</td>
<td>7.99</td>
<td>41.55</td>
<td>41.127</td>
</tr>
<tr>
<td>1.382</td>
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</tr>
<tr>
<td>1.157</td>
<td>1.70</td>
<td>3.29</td>
<td>6.279</td>
</tr>
<tr>
<td>1.052</td>
<td>0.34</td>
<td>2.07</td>
<td>3.514</td>
</tr>
</tbody>
</table>

Table 1. The szomolnokite percentage in the samples

As it is shown in the table, tendency to decreasing both with increasing of szomolnokite content with decreasing S/Fe ratio is observed both X-ray data and the theoretical calculation results.

Seasonal magnesium isotope variations in soil solutions reflecting physico-chemical processes controlling soil weathering fluxes

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Chemical weathering supplies base cations controlling the long-term availability of nutrients. Base cations, including magnesium, lost by plant uptake or leaching, are replaced by mineral weathering and partly retained on the soil exchange complex. Despite Mg isotopes being used as a weathering proxy, the fractionation mechanisms in the critical zone are still unclear. Here we report the first look into the seasonal variability of Mg isotope compositions in soil solutions derived from a well-defined protolith, Icelandic basalt, which was exposed to seasonal freeze-thaw cycles. Less weathered freely drained Brown and Gleyic Andosol (BA-GA) are compared with more weathered poorly drained Histosol and Histic Andosol (H-HA). The difference in clay content (35 and 48%) and proportions of exchangeable Mg (2 and 7%) in BA-GA and H-HA, respectively, allow for a direct assessment of the processes controlling Mg isotope ratios ($^{26}$Mg relative to DSM-3). Vegetation (-0.30 to -0.18‰) is heavier than parental basalt (-0.31‰) and bulk soils (-0.79 to -0.25‰). Soil solutions (-1.16 to -0.53‰) are relatively lighter than the basalt. Magnesium retention on the soil exchange complex is larger in neutral than in acid soils and discriminates against light Mg isotopes (-0.88 to -0.51‰) contributing towards isotopically lighter soil solutions in BA-GA. Seasonal variations (from June to September) of Mg isotope ratios in soil solutions from organic-rich H-HA are likely to reflect the release of heavier Mg isotopes from the decomposition of plant material during thaw. Our results show that Mg isotopes have a great potential as a proxy for seasonal soil processes, especially in sub-arctic soils where environmental changes would potentially affect vegetation decomposition, CO2 release, and associated nutrient delivery to the hydrosphere.
Erebus: A laboratory volcano in Antarctica

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Erebus, the only presently erupting phonolite volcano, offers an exceptional opportunity to examine the complexities that accompany degassing and the evolution of magmas from deep to shallow levels. These include aspects of magma differentiation, redox chemistry and eruptive transitions widely relevant to understanding other volcanoes. Its long-lived anorthoclase phonolite lava lake, sustained degassing and hyperarid environment provide uncommonly favourable circumstances for direct measurement of the lava lake – the uppermost portion of the magmatic system.

Several features distinguish Erebus: the decidal persistence of the lava lake; evidence for continuous fractionation (the Erebus Lineage) from basanite to phonolite; episodic Strombolian activity at the lava lake (which provides samples for analysis); and the abundance of megacrysts (up to 10-cm-long) of anorthoclase feldspar in the lava lake. The longevity of the lava lake implies counterflow of vesicular and hyperarid environment provide uncommonly favourable circumstances for direct measurement of the lava lake – the uppermost portion of the magmatic system.

Halophilic microorganisms: Modern and ancient, on Earth and in Space

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Salt-saturated environments on Earth are inhabited by a great diversity of halophilic microorganisms. They are found in all three domains of life: Bacteria, Archaea, and Eucarya. Many can thrive not only at low water activities, but are also adapted to high divalent cations concentrations (the Dead Sea) and to extremes of pH and temperature. Different groups of halophiles can be detected using biomarkers such as the archaeal isoprenoid ether lipids, pigments (the archaeal C-50 bacterioruberins, β-carotene from the alga Dunaliella salina), and osmotic solutes such as glycine betaine and ectoine in Bacteria, glycerol in Dunaliella.

When halite crystallizes from salt-saturated brines, microorganisms are often trapped within fluid inclusions in the crystals, where they can survive for prolonged periods. Live microorganisms have been recovered from ancient halite, e.g. Virgibacillus marismortui from Permian salts of New Mexico, Archaea (Halobacterium, Natronobacterium) from Cretaceous halite crystals from Brazil. DNA encoding bacterial and archaeal RNA genes was recovered from Cretaceous (Brazil) and Silurian (Michigan) salt. Salt crystals were preserved in Death Valley, CA, contained microscopically recognizable prokaryotes, as well as Dunaliella, which may have provided the prokaryotes with glycerol and other organic compounds as a source of energy for survival. In spite of the earlier scepticism, compelling evidence for long-term survival of halophilic microorganisms within salt crystals has accumulated in the past decade.

Some species of halophilic Archaea can survive large doses of UV radiation, desiccation and exposure to low temperatures, but not all halophiles are equally adapted. Some strains of halophilic Archaea have survived flights on the Biopan facility of the space shuttle, including a species named Halorubrum chaovittii, ‘the traveller of the void’.

Halite has been detected on Mars and in meteorites. In view of the ability of some halophiles to survive in salt at low water activity, high radiation levels, and in a broad range of pH, salt crystals are promising material to search for life elsewhere in the universe, using a combination of techniques: microscopy, gene-based approaches, and detection of specific biomarkers. Model systems on Earth – recent and ancient – provide plentiful material to evaluate the different methods.

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Numerical study of weathering fluxes at the catchment scale in a boreal watershed: A coupled thermo-hydro-geochemical mechanistic approach

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This work deals with the assessment of the impact of the climatic changes on weathering processes in boreal catchments which are characterized by the occurrence of a continuous permafrost. The two main goals of this study are: (i) to quantify the influence of seasonal cycles of freezing and thawing of the active layer on the fluxes of chemical elements generated by the weathering processes and (ii) to estimate the effect on the weathering fluxes of possible interannual variations of these cycles caused by climatic changes. Our approach is based on the development and the validation of a coupled thermo-hydrological mechanistic modelling at the catchment scale for current climatic conditions. This thermo-hydrological model is designed to give the entrance data (the seasonal evolutions of the average thickness and of the average water content of the active layer) for the computation of weathering fluxes with the WHITCH geochemical model (e.g. [1]). This modelling approach at the catchment scale is established on the basis of the data available in the International Research Group CAR WET SIB ([2], [3]). In further studies, the model developed here will allow to forecast the impact of various scenarios of climatic changes on the weathering fluxes.


Geochronological fingerprint revealed the evolution of the crust underlying Cerro Pampa adakite, Argentine Patagonia

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We reports the results of U-Pb dating for 282 zircon crystals separated from a Middle Miocene adakite in Cerro Pampa, southern Argentine Patagonia, using LA-ICP-MS. With the exception of 3 spot ages, 140 of the concordia ages are significantly older (> 94 Ma) than the cooling ages of the adakite magma (~ 12 Ma). Kay et al. [1] attributed the origin of adakite magmas to partial melting of subducted slab of the Nazca plate. Presence of exotic zircon crystals clearly indicates crustal contaminations to produce the adakitic magma in Cerro Pampa. The obtained concordia ages of exotic zircons range from 94 Ma to 1441 Ma and could be divided into five groups having distinctive peaks on a population diagram. The first (100-125 Ma) and second age groups (125 to 145 Ma) correspond to the age of plutonic activities that formed main body of the South Patagonian Batholith [2]. The third to fifth groups correspond to activities of El Qumado-Ibañez volcanic complex (145-170 Ma) [2], gabbroic rocks scarcely distributed in Central Patagonia (170-200 Ma), and the Eastern Andean metamorphic complex of Late Paleozoic to Early Mesozoic ages (200-380 Ma) [3], respectively.

Our data suggests that the crust underneath Cerro Pampa were mostly formed after 380 Ma and majority of the upper crust was formed during early Cretaceous to middle Jurassic. The processes of crustal development ceased ~ 94 Ma until the activity of the Cerro Pampa adakite in ~ 12 Ma. There was no evidence for Archean-Paleoproterozoic crust.

Microbial partnerships and methane-oxidation in the deep sea

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The ability to decipher the metabolic roles of microorganisms within living microbial ecosystems and to connect microbial metabolism with biosignatures preserved in the rock record represents some of the grand challenges in the field of Microbial Geobiology. The combination of molecular methods with stable isotope analysis (both natural abundance and as tracers) in modern environments represents a multidisciplinary approach that has been used successfully to characterize links between specific microorganisms and their ecophysiology in situ. In particular, the introduction of micron-scale isotopic analyses by secondary ion mass spectrometry (SIMS and nanoSIMS) [1] to the study of microorganisms has enabled an unprecedented level of inquiry into the inner workings of microbial ecosystems. Integrating SIMS-based stable isotope analysis with microscopy and culture-independent metagenomics techniques, we have been investigating carbon and nutrient utilization by deep-sea microorganisms and symbiotic microbial consortia fuelled by methane in sediments and associated authigenic carbonates. Single cell characterization of methane-cycling archaea and sulphate-reducing bacteria have revealed significant inter and intra-group heterogeneity in both stable carbon isotopic signatures and nitrogen utilization, including differences in nitrogen fixation [2] and assimilatory nitrate reduction. These cell-specific analyses have yielded new information regarding the isotopic variability, metabolic potential and interactions between individual microorganisms and the greater biological community in methane-based ecosystems.


Combining electrochemical and spectroscopic methods to obtain speciation of quinones

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In anoxic aquifers, the presence of goethite-Fe(II) systems plays a major role in electron transfer processes, such as degradation of organic pollutants [1]. To investigate the role of organic matter as potential electron shuttles commonly model quinones such as AQDS, juglone and lawsone were used [2, 3]. To address this question we studied interactions with iron minerals and the speciation of model quinones.

Defined redox and acid-base species of the model quinones were obtained by electrochemical methods, varying systematically the reduction potential, pH and ionic strength. The UV-visible spectra of these species were used as reference to obtain the redox speciation of quinones in goethite-Fe(II) systems. From these data information on electron transfer processes, redox potential and equilibrium states of the redox sensitive quinone and iron species can be derived.

PGE distribution in base-metal sulfides from the Merensky Reef of the Bushveld Complex, South Africa

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Introduction
Several studies were undertaken to elucidate the distribution of PGE between various sulfides such as pentlandite, pyrrhotite or chalcopyrite [1, 2]. This present study concentrates on the PGE distribution in BMS in profiles of the Merensky Reef of the Bushveld Complex using whole-rock, electron microprobe and LA-ICP-MS analysis.

Results
Pentlandite is a principal host of Pd (and Rh) whereas Pt is mainly hosted by PGM. The distribution of Pt and Pd in two profiles from the western Bushveld reveals a top-loaded mineralization – max. concentrations of Pd and Pt occur in the area of the upper chromite stringer in the whole-rock, coinciding with max. concentrations of Pd in pentlandite (Fig. 1). Two profiles from the eastern Bushveld reveal ‘offset patterns’ – max. concentration of Pd in pentlandite is displaced ny 0.5 – 1 m below the max. concentration of whole-rock Pd and Pt. Downward percolation of sulfides or post-magmatic processes such as selective diffusion may be responsible for the observed offset feature.

Figure 1: Pd and Pt distribution in pentlandite and whole-rock.

The evolution of surface, intermediate and deep water connections during the closure of the Central American Seaway

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The progressive closure of the Central American Seaway and the associated reorganisation of deep-ocean circulation have been controversially reported as contributing to a warming and a cooling of global climate, as well as increasing moisture supply to the northern hemisphere and hence preconditioning the inception of Northern Hemisphere Glaciation. Here we use radiogenic isotopes of Nd and Pb to reconstruct the history of shallow, intermediate and deep water connections between the Caribbean Sea and the eastern Equatorial Pacific Ocean from 5.0 to 2.0 million years ago. Surface water exchange and mixing is characterised using the Nd isotope composition of planktonic foraminiferal calcite. The Nd and Pb isotope compositions of early diagenetic ferromanganese coatings of the same sediment samples are employed to determine intermediate and deep water exchange.

A core-top survey compares $E_{dw}$ in surface sediments, with the expected water mass signature. Leaches of core-top sediments taken from intermediate water depths (~1000m) in the central Caribbean Sea give values between $E_{dw} = -7.5$ and -10.2. Planktic foraminifera from the same samples have $E_{dw}$ between -8 and -10.8. Around a deeper central Caribbean site (~3000m), leaches give between -5.9 and -8.2 in $E_{dw}$, which is 2 to 6 $E_{dw}$ units more radiogenic than published data from ferromanganese crusts in the Lesser Antilles [1, 2], but still significantly less radiogenic than core-top leaches from the Eastern Equatorial Pacific (EEP), which have $E_{dw}$ between 2 and 0. These latter measurements are broadly consistent with data from an EEP ferromanganese crust [3]. These findings form the basis for the down-core survey and the reconstruction of the exact timing of the closure of the seaway and corresponding water mass exchange at different water depths.


References
3 stages of Earth evolution — Core formation, ocean emergence and the 2.3 Ga rise of atmospheric oxygen: How are they linked?

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Recognized nearly a century ago [1], the mean specific angular momentum (a. m.) of SS planetary materials is $>10^5$ times the Sun’s, so it is an important constraint upon how the planets were built. Nebula is the only conceivable agent for this partition. And it must do this for both the protoplanet and all of its feedstock, so planetary growth must be essentially complete before it departs (<5 Ma?). This rules out the post-nebula growth in cores-by-Fe-percolation models, for which isotopic (Hf-W, etc) data have been interpreted as needing upwards of 30 Ma for completion, though this interval may actually relate to post-core-completion exchange at the CMB.

Those models also do nothing for the origin of SS water. Ringwood’s model (1960-1978) invokes a cool nebula, achievable with other advantages [2-4], to give high-$\delta^{18}$O. This rules out the post-nebula growth in cores-by-Fe-percolation models, for which isotopic (Hf-W, etc) data have been interpreted as needing upwards of 30 Ma for completion, though this interval may actually relate to post-core-completion exchange at the CMB.

But at ~2.49Ga, ocean production caused parts of the upper mantle to reach a critical loss of water-weakening in the presence of interstitial melt [5], halting convective motion for ~270Ma [6, 7]. MOR collapse lowered sea-level by >3km, exposing cratons to erosion, unroofing TTG, lowering atmospheric CO2 and causing Huronian glaciation (2.4 Ga).

During this hiatus, oxygenic life, previously confined to the deep-keeled tectospheres of stiffened mantle, lost the means to escape. The restart after 2.22Ga left cratons with a more complex dependence. Besides primary precipitation phase transition of calcium sulfate in contact with the mother solution occurs over time (>days). With time the temperature at which bassanite and anhydrite appear decreases. This behavior is generalized for the three salinities studied but at the highest salinity this phase transition occurs faster.

A plausible explanation for the mechanism of phase transition is the dissolution of the phase that precipitates first (less stable) and subsequent ‘recrystallization’ of the more stable phases with passing time. The kinetics of dissolution/precipitation of these compounds plays a decisive role in the transition rates of calcium sulfate phases and are mainly controlled by temperature and solution salinity.

Experimental study of nucleation and phase stability of calcium sulfate

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Calcium sulfate presents three common phases when precipitated from aqueous solution in nature or in the laboratory: gypsum (CaSO$_4$$\cdot$2H$_2$O), bassanite (CaSO$_4$$\cdot$0.5H$_2$O) and anhydrite (CaSO$_4$) [1]. The conversion of these phases into each other takes place in nature but also represents the basis of gypsum-based building materials. Therefore many studies have been performed on the phase stability of calcium sulfate in solution, as a function of temperature but, at present, the mechanisms by which precipitation, phase transition and phase stability occur in solution are not well defined [2].

We performed an experimental study in order to identify the factors that influence the nucleation, growth and phase stability of calcium sulfate at laboratory scale. The crystallization was carried out by chemical reaction by varying temperature (40°C-120°C), salinity (0.8, 2.8, 4.3 M NaCl) and duration of the experiments (2 min – 3 months). The reaction products were characterized by Powder X-Ray Diffraction, SEM and TEM.

Our results show a clear dependence on temperature and salinity of the precipitated phase of calcium sulfate; at low temperatures, gypsum is the most stable phase (<60°C). As temperature increases, direct precipitation of bassanite (80-110°C) and anhydrite (120°C) occurs. The temperature at which primary bassanite appears decreases with increasing salinity (110-80°C) while anhydrite shows a more complex dependence. Besides primary precipitation phase transition of calcium sulfate in contact with the mother solution occurs over time (>days). With time the temperature at which bassanite and anhydrite appear decreases. This behavior is generalized for the three salinities studied but at the highest salinity this phase transition occurs faster.
Petrogenesis of syn-orogenic leucogranites (Damara orogen, Namibia)

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The granite-dominated part of the Central Damara Orogen (Namibia) consists of basement gneisses, high-grade metamorphic metasedimentary rocks, and crust-derived granites. Granites that crop out in the Kubas area fall into two groups; 553±8 Ma-old grey granites and 513±6 Ma-old red leucogranites. The grey granites have a common granitic composition but the red leucogranites are highly fractionated melts shown by extremely high Rb/Sr ratios, fractionated REE patterns and the presence of euhedral Mn-rich garnet. Digested remnants of upper crustal pelites are clusters of biotite, sillimanite and cordierite indicating some crustal contamination. The grey granites have less evolved isotopic compositions (init. 87Sr/86Sr: 0.720; init. 143Nd: -16; large variation in ²⁰⁶Pb/²⁰⁴Pb (15.55-15.61) at ²⁰⁶Pb/²⁰⁴Pb ratios lower than the red leucogranites). The red leucogranites have more evolved isotopic compositions (init. 87Sr/86Sr: 0.725-0.750; init. 143Nd: -16; large variation in ²⁰⁶Pb/²⁰⁴Pb trending towards the composition of common pelitic metasediments from the Damara orogen). These isotopic features indicate that both granite types represent melts from a similar source (Proterozoic/Archaean basement?) but have undergone different processes. The grey granites appear to be uncontaminated and hence, their composition mirror their sources. The red leucogranites have apparently interacted with upper crustal rocks via AFC processes (digested xenoliths, fractionated REE patterns, large variation in Sr and Pb isotopes), probably during stagnation within the crust. Such lower crustal melts are apparently confined to the pre-to syn-collisional phase of the orogeny and it is therefore likely that they have also contributed to the heat budget that controlled high-temperature metamorphism. Even in complex terranes granites can preserve a record of their sources and can be used to place limits on possible compositions of the unexposed sources of the granites and thus on the nature of the terranes through which the melts ascended.

Level of ¹²⁹I and ¹²⁷I in terrestrial environment of Slovenia: A two-year study of background areas

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Introduction

Iodine has two natural isotopes – ¹²⁷I is a stable isotope, while ¹²⁹I is a radioactive isotope formed naturally by spallation of cosmic rays on atmospheric Xe and spontaneous fission of ²³⁸U. However, the main sources of ¹²⁹I in the environment are anthropogenic from nuclear fuel reprocessing plants (NFRP). Current levels of ¹²⁹I do not represent any radiological hazard to humans, but the discharges of ¹²⁹I from NFRP can be used as an environmental tracer [1]. Our aim was to investigate levels of ¹²⁹I in environment of Slovenia, because no data exist.

Experimental

Samples of precipitation, soil from opened field and forest, and pine needles were collected three times at four various locations in period 2009–2010. Total concentrations of ¹²⁷I and ¹²⁹I were determined with radiochemical neutron activation analysis [2].

Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>¹²⁹I (µg g⁻¹)</th>
<th>¹²⁹I/¹²⁷I (10⁻⁸)</th>
</tr>
</thead>
<tbody>
<tr>
<td>precipitation (n = 10)</td>
<td>0.0017–0.0065</td>
<td>&lt;2.3–91.0</td>
</tr>
<tr>
<td>soil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>opened field (n = 12)</td>
<td>2.4–22.2</td>
<td>0.7–7.1</td>
</tr>
<tr>
<td>forest (n = 12)</td>
<td>3.9–35.2</td>
<td>0.7–7.4</td>
</tr>
<tr>
<td>pine needles (n = 12)</td>
<td>0.058–0.413</td>
<td>15–189</td>
</tr>
</tbody>
</table>

Table 1: Range of concentration levels and ¹²⁹I/¹²⁷I ratios

Discussion

The highest concentrations of ¹²⁷I and ¹²⁹I were found in soil samples. Soil samples collected in forest, where more organic matter is present; contained more ¹²⁷I and ¹²⁹I than soil from opened field, although the ¹²⁹I/¹²⁷I isotopic ratio is the same. The highest ¹²⁹I/¹²⁷I isotopic ratio was found for pine needles. Obtained results are the first for terrestrial environment of South Europe and are comparable to values found in literature for background areas.

Transformation of nitrogen during sediment burial history
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Many gas reservoirs contain appreciable percentages of gaseous dinitrogen besides the commercial valuable hydrocarbon gases. The source of this nitrogen and its transformation path to gaseous dinitrogen is still a matter of ongoing research (cf. [1], [2]).

To follow the transformation of nitrogen in organic rich sediments and sedimentary rocks during burial history with increasing pressure and temperature different approaches have been followed in this study: (1) Two sets of natural maturity series of type II or type III kerogen containing sediments and sedimentary rocks have been analysed with respect to several forms of nitrogen: exchangeable NH4+, N in the bitumen, HCl-hydrolysable N (amino-N in kerogen and N in clay minerals), kerogen bound N and N fixed in feldspars and other acid-stable minerals. In addition to the concentrations of the different nitrogen forms the nitrogen isotopic composition was investigated. (2) For the low maturity sediment and sedimentary rock samples artificial heating experiments in closed gold capsules as well as in flexible gold-titanium cells at high pressures and temperatures have been conducted to simulate the natural maturation process.

The results clearly document the release of organically bound nitrogen during early maturation – and a concomittant increase in dissolved inorganic nitrogen concentrations. With elevated ammonium concentrations in the pore water the incorporation of ammonium into authigenic minerals increases. This mineral-bound nitrogen is fixed until the mineral phase is destabilised by higher p-T-conditions or changing aqueous fluid compositions. The final transformation of ammonium released from minerals to gaseous dinitrogen might be a consequence of redox reactions involving mineral surfaces. At very high temperatures dinitrogen might be formed from organically bound nitrogen in type III kerogen.


U-Pb and Pb-Pb dating of phosphates in Martian meteorites
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There are many studies that measured U-Pb and Pb-Pb ages in phosphates of Martian meteorites. The ages of Shergottites are controversial, ranging from 4 billion years [1] to 200 million years [2] and are not well constrained. The ages are very important for understanding Martian evolution.

Here we show the U-Pb and Pb-Pb ages in several Martian meteorites. ALH84001, Zagami, DaG476 and some other Martian meteorites were investigated. For U-Pb and Pb-Pb dating by NanoSIMS, primary O- ions with a beam intensity of 10nA were used in a spot diameter of about 10-20 micrometer. An apatite from Prairie Lake called PRAP with a known age [3] was used as a standard for Pb/UO-UO2 calibration. The age of ALH84001 is about 4 billion years and it is consistent with those of the previous studies [4] within the experimental error. Our U-Pb age of phosphate minerals in Zagami are very young, suggesting that it was reset by some recent metamorphism. However the Pb-Pb isochron age at the same spots of U-Pb dating is about 4 billion years. This age is derived from two grains. Our data suggest that Zagami crystallized at 4 billion years ago, and it experienced some recent metamorphism to reset the U-Pb age. At the poster session I will discuss the implication of the U-Pb and Pb-Pb ages of ALH84001, Zagami and other Martian meteorites.

Origins of chromite found in chemical and clastic sedimentary rocks of the 3.2 Ga Moodies Group, South Afrirca

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The timing of the emergence of oxygenic photoautotrophs (e.g. cyanobacteria) is critical for understanding the evolution of life and the earth’s surface environments. Yet, no palaeontological or geochemical signature in sedimentary rocks has provided unequivocal evidence for the emergence of cyanobacteria in the Archean era. The objective of this study was to find mineralogical and geochemical signatures that mark the emergence of cyanobacteria in a shallow ocean environment from the the Moodies Group, South Africa (~3.2 Gyr), in which Javaux et al. (2010) [1] discovered large, well-preserved microfossils, possibly the remnants of eukaryotes. We were particularly focused on the origins of chromite (FeCr2O4) and magnetite (Fe 3O4), which contain the redox-sensitive elements, iron (Fe) and chromium (Cr), found in the chemical and clastic sedimentary rocks.

Our samples collected from underground mines (e.g. Sheba gold mine) were divided into 3 groups, based on the dominant iron-bearing mineral: the Siderite (FeCO3), Magnetite, and Hematite (Fe2O3) groups. While fine-grained (<50 μm in diameter) hematite, or ferric hydroxide (Fe(OH)3) as its precursor, was interpreted to have been directly precipitated from seawater, large-grained (>50 μm in diameter) magnetite and siderite were interpreted to have formed during early diagenesis. We identified two types of chromite: eudheral and unhedral chromite. All eudheral chromite, which was observed in the Magnetite group, was overgrown by magnetite. This suggests that both euhedral chromite and magnetite in the Magnetite group were formed during diagenesis. On the other hand, unhedral chromite in the Siderite group was often included in silicate minerals (e.g. chlorite and biotite), indicating that it is detrital in origin. A positive correaltion between the Cr/Ti ratio and the U/Th ratio in the bulk chemical composition of the Magnetite group may suggest that both Cr and U were transported to the ocean through oxidative chemical weathering, and therefore that cyanobacteria was emerged before 3.2Ga.


Uranium speciation in opals from the Nopal I deposit (Mexico)

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The study of uranium migration and trapping in the environment is relevant to assess the safety of potential high-level nuclear waste repositories (HLNWR). The Nopal I uranium deposit (Sierra Peña Blanca, Mexico) is a natural analogue of HLNWR located in volcanic tuff. Secondary uranyl minerals such as uranophane and weksite occur in the deposit and are coated by opal [1],[2].

The aim of this study is to determine the uranium speciation in these opals to reveal the low temperature conditions of trapping of this element, from the micrometer scale of electron microscopy to the molecular scale provided by fluorescence spectroscopy.

Uranium speciation was found to be various and complex. We evidenced by scanning electron microscopy (SEM) microparticles of β-uranophane Ca[(UO2)2(SiO3OH)](H2O)5 and apatite Ca5(PO4)3(OH, Cl, F) containing small amounts of uranium. However the major part of uranium is concentrated in Ca-U-enriched zones with a Ca:U ratio of 1:1 and displaying spherical features (Fig. 1).

Figure 1: SEM back-scattered electron picture of a yellow opal cross-section from the Nopal I uranium deposit, Mexico.

The exact nature of Ca-U species in these zones was not determined but transmission electron microscopy (TEM), cathodoluminescence and time-resolved laser fluorescence spectroscopy (TRLFS) analyses suggest the presence of Ca5(UO2)3(OOH/H2O)6 complexes adsorbed or incorporated in opal. These results will be discussed in terms of chemical conditions that prevailed during U incorporation.

Density functional theory study of the interaction of arsenic complexes with FeOOH surfaces

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Iron oxyhydroxides (FeOOH) possess high surface areas which are relevant for cycling and retention in a series of environmental and technological processes [1]. Using density functional theory (DFT), we explore the stability and electronic properties of the goethite (101), akaganeite (100), and lepidocrocite (010) surfaces under different environmental conditions. The GGA+U calculations reveal that the termination impacts the oxidation state of the surface iron ions, providing a possibility to tune the catalytic activity. The energetics and bonding mechanisms of arsenic complexes in different adsorption geometries (e.g. mono- and bidentate) on the surfaces are investigated.

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Quantification of primary marine organic aerosol properties using aerosol mass spectrometry

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Marine aerosol has a strong impact on both the Earth’s albedo and climate; however, its inherently complex composition ranging from inorganic components (sea salt, nss sulfate) to complex organic carbon mixtures of water soluble and insoluble components [1, 2] and bioaerosol components [3] complicates the quantification of those impacts. In recent years, the dominant organic matter (OM) contribution (in particular, the primary organic matter) to submicron marine aerosol during periods of high biological activity over N.E. Atlantic has been quantified on a seasonal basis [1] as well as in real-time [4]. However, the character of its influence on cloud formation is still undergoing an intense discussion. Here, we present the comprehensive long term real time ambient aerosol measurements which reveal the important role of marine organics to cloud formation: the recurrent enhancement of cloud formation activity (cloud condensation nuclei) under aerosol enrichment by primary organics with low hygroscopic growth factor is reported for the first time. Moreover, the complexity of organic matter identified by high resolution time of flight aerosol mass spectrometry (HR-ToF-AMS) and its interpretation from HR-PMF (Positive matrix factorization) revealed a dominant contribution of primary sources to marine organic aerosol, with unique marine organic aerosol fingerprint, when compared to anthropogenic organic aerosol.

First principles investigation of manganese oxide surface chemistry

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Manganese oxides, which are ubiquitous in geological settings, play an important role in heavy metal adsorption and oxidation in the environment. In particular, the ability of manganese oxides to oxidize trivalent chromium to hexavalent chromium has garnered considerable attention, but questions remain concerning the mechanism of oxidation. To accurately model hexavalent chromium transport and its fate in the environment, the specific interactions between chromium ions and manganese oxide surfaces must be ascertained. Because structure, composition, and chemical properties of surfaces are intimately related to reactivity, a fundamental understanding of manganese oxide surface reconstructions and redox behavior lays the foundation for investigating oxidation mechanisms involving manganese oxides. However, detailed structural analyses of manganese oxide surfaces under environmentally relevant conditions are scarce.

We have combined periodic density functional theory calculations and ab initio thermodynamics to identify stable surface terminations of the \( \beta\)-MnO\(_2\) (110) and \( \gamma\)-MnOOH (010) surfaces and to determine their redox behavior in response to varying oxygen and water chemical potentials. Reduction of the surfaces produces interesting surface reconstructions driven by the competition between lattice constraints and optimal \( d\) orbital occupation and manganese coordination geometry. Multiple oxidation states are found at the surfaces due to Jahn-Teller effects. Under ambient conditions, oxidation of the \( \gamma\)-MnOOH (010) surfaces is predicted to be favorable, while the reduced \( \beta\)-MnO\(_2\) (110) and \( \gamma\)-MnOOH (010) surfaces are not stable but may become relevant during heavy metal oxidation processes at the surface. Molecular and dissociative adsorption of water on the clean surfaces significantly lower the surface free energies. Binding sites for trivalent chromium on the hydrated surfaces will be presented with a focus on the effect of manganese oxidation state on adsorption geometry.

Modeling oceanic anoxia/euxinia induced by massive CO\(_2\) injection

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Atmosphere-ocean biogeochemical cycle model

Rapid global warming caused by large igneous provinces (LIPs) has been suggested as the cause of ocean anoxia. To constrain the required conditions for the occurrence of oceanic anoxic event (OAE) and investigate the climate change during OAE, we constructed the atmosphere-ocean biogeochemical cycle model. The ocean model [1] can reproduce the vertical distribution of several dissolved components (e.g. PO\(_4\), O\(_2\), H\(_2\)S, DIC, Alk) in the water column. We also consider the kinetic treatment of carbonate dissolution in the ocean. Hence, carbonate compensation depth (CCD) can also be calculated. The simplified chemical (carbonate and silicate) weathering on land and air-sea exchange of CO\(_2\) were also included.

Results and discussions

We conducted the sensitivity analyses of CO\(_2\) injection event systematically with several initial conditions (we especially focused on \( p\)CO\(_2\), \( p\)O\(_2\), SST, and shelf area) because climate and geographical setting would affect the required amount of CO\(_2\) and behaviour of climate change. Simulations indicate that (1) enhanced nutrient (phosphorus) input to ocean effectively promote the oceanic productivity, resulting in an expansion of oxygen minimum zone and nutrient efflux from the surface sediments to the bottom waters, (2) global eutrophication (and anoxia) can be induced by a positive feedback loop among anoxia, phosphorus regeneration, and surface productivity, (3) once global anoxia achieve, enhanced accumulation of organic carbon in marine sediments acts as a buffer against global warming, resulting in climate cooling during OAE in some cases.

In this presentation, we will also discuss the effect of initial conditions on the required amount of CO\(_2\) for the occurrence of global anoxia. We conclude that historical background has an important role in the required conditions for OAEs.

Petrographic and geochemical characteristics of dolomites in the Golbogazi Formation (Upper Devonian) at SW of Hadim, (Konya - Turkey)

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Upper Devonian units, locating Central Taurus composed of thick dolomite with massive limestones layers and thinner dolomite layers with intercalated limestone are described. Various dolomite types include: Type I) dolomite formed as dolomicrite as mimic replacement, Type II) the planar- texture dolomites are scattered in a micritic matrix, Type III) fracture and void filling dolomite (zoned dolomite, overgrowth and saddle), Type IV) brecciated dolomite, and V) polymodal dolomite.

The Sr content in the Golbogazi Formation (184 to 74 ppm in the early dolomites, and 105 to 78 ppm in the late dolomites, respectively) is compatible with the Sr concentration mixing-zone dolomites. The Na content in the Golbogazi Formation (593 to 148 ppm in the early dolomites, and 519 to 297 ppm in the late dolomites, respectively) is compatible with the Na concentration mixing-zone dolomites.

The investigated dolomites exhibit -1.95 to -3.46 PDB in $^{18}$O values relative to their $^{13}$C values (1.33 to -1.33 PDB) in the early diagenetic dolomites. The late diagenetic dolomites display -3.96 to -9.44 PDB in $^{18}$O values relative to their $^{13}$C values (2.52 to -1.58 PDB).

As a result, the Golbogazi Formation dolomites have been formed as early diagenetic at the shallow marine environment and as the late diagenetic at the shallow-deep burial depths.

Comparison of REE concentrations between the Bozkir ophiolitic rocks and stream sediments derived from these rocks in the Bozkir Region (Konya – Turkey)

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The study area located in south and east of Bozkir (Konya-TURKEY), covers approximately 250 km². The units cropped out in the study area are Geyikdağı (slightly metamorphic detritic and carbonaceous rock), Bozkir (ophiolitic rocks such as serpentinite, pyroxenite, gabbro, radiolarite, chert, limestone) and Bolkardağı (generally limestones) tectonic units from bottom to top. This study aims investigation of REE concentration of the rocks and stream sediment samples derived from Bozkir Ophiolitic Melange and comparison between the two mentioned groups [1, 2].

REE contents of the rock samples higher than those of the chondrite and peridotite while lower than that of NASC. REE, HREE (La-Sm) and LREE (Gd-Lu) of the rocks are 112.2, 97 and 15.2 ppm respectively. REE contents of stream sediments higher than that of the rock samples (Table 1).

Table 1. REE contents of the rock and stream sediment and normalized values to the some reference rocks.

<table>
<thead>
<tr>
<th>REE</th>
<th>Samples</th>
<th>Normalized values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rocks</td>
<td>Str. Sed.</td>
</tr>
<tr>
<td>La</td>
<td>22.1</td>
<td>24.1</td>
</tr>
<tr>
<td>Ce</td>
<td>44.8</td>
<td>49.2</td>
</tr>
<tr>
<td>Pr</td>
<td>5.4</td>
<td>5.3</td>
</tr>
<tr>
<td>Nd</td>
<td>20.7</td>
<td>20.3</td>
</tr>
<tr>
<td>Sm</td>
<td>4.1</td>
<td>4.1</td>
</tr>
<tr>
<td>ΣREE</td>
<td>97.1</td>
<td>103</td>
</tr>
<tr>
<td>Eu</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Gd</td>
<td>3.7</td>
<td>3.8</td>
</tr>
<tr>
<td>Tb</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Dy</td>
<td>3.8</td>
<td>4</td>
</tr>
<tr>
<td>Ho</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Er</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>Tm</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Yb</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>Lu</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>ΣREE</td>
<td>15.2</td>
<td>16</td>
</tr>
</tbody>
</table>

The investigated dolomites exhibit -1.95 to -3.46 PDB in $^{18}$O values relative to their $^{13}$C values (1.33 to -1.33 PDB) in the early diagenetic dolomites. The late diagenetic dolomites display -3.96 to -9.44 PDB in $^{18}$O values relative to their $^{13}$C values (2.52 to -1.58 PDB).

Some normalized values of the rock samples to the chondrite such as La/Lu, Gd/Yb, Eu/Eu* and Ce/Ce* are 5.44, 1.27, 0.68 and 0.93.

Mineralogy and geochemistry of the Yellice magnetite occurrences of Sivas-Central Anatolia, Turkey

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Ophiolitic rocks, trusted tectonically over Munzur limestones of Taurus platform and emplaced during Maastrichtian form the basement of the study area.

The primary ore mineral at Yellice is magnetite in serpentinized ultramaphic rocks of ophiolites. Other ore minerals are chromite, machinavite inclusions bearing pentlandite, pyrrhotite, cubanite lamellae bearing chalcopyrite and pyrite characterizing a liquid magmatic phase. Secondary magnetites of a subsequent phase are formed from ferromagnesian minerals during serpentinization processes.

XRD studies carried on post-tectonic basin deposits (e.g. basalts) indicate albite, calcite, augite, chlorite, olivine and lizardite minerals which point out to minerals occurred by ocean floor metamorphism [1]. Two different mineral assemblages occur in serpentinites. The first paragenesis is antigorite, talc, magnetite, magnezite and chlorite which indicate nearly 400-500 °C temperature conditions [2]. The second paragenesis represented by chrysotile, lizardite, diopside, augite, tremolite, actinolite, calcite, quartz, chromite, magnetite, olivine and talc characterize approximately 350-400°C temperatures and suggests an ocean floor (or hydrothermal) metamorphism [3].

Raman studies revealed that the plagioclases of basaltic rocks are albitized by the affects of sea water. Some pyroxenes are replaced by actinolites due to uralitization.

Consequently, lens shaped magnetite ores with an average grade of 18-20 % Fe₃O₄ and 125 millions tons of tonnages in serpentinites suggest an assemblage of primary minerals formed in upper mantle conditions and a further element association by serpentinization processes.