Paleoclimatic changes across the Cretaceous-Paleogene boundary: Geochemical reconstructions from Seymour Island, Antarctica

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The Cretaceous-Paleogene (K-Pg) boundary, ~66.0 Ma, marks the most catastrophic global extinction event of the past 100 Myr and is well documented in both terrestrial and marine biotic records. Although the K-Pg mass extinction occurred at a time when the Earth’s climate operated under greenhouse conditions, the specific climatic and environmental changes associated with this event remain poorly understood. Shallow marine sediments exposed on Seymour Island, Antarctica (paleolatitude ~65°S) provide one of the most expanded K-Pg successions known. Moreover, the high latitudes represent areas of significant climatic importance due to polar amplification of global warming.

We first present a low resolution MBT/CBT (methylation of branched tetraethers/cyclisation of branched tetraethers) continental temperature reconstruction that indicates a persistent cool temperate climate (11.4 ±5 °C) on the Antarctic Peninsula during the latest Cretaceous to early Paleogene. The addition of a higher resolution study across the K-Pg boundary is then used to investigate short-term paleoclimatic and paleoenvironmental perturbations, using MBT/CBT, BIT indices and biomarker abundances. Integration of these data with paleontological and paleobotanical datasets allows us to reconstruct the response and recovery of high latitude terrestrial and marine environments to the K-Pg global extinction event.

Reaction mechanisms, pathways, and transport in anaerobic abiotic and microbial U(IV)-oxide dissolution studies

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Applications of combined thermodynamic-kinetic descriptions to mineral-water interface processes that include chemical reactivity, microbial metabolism, and physical transport are challenged by the need to bridge differences in spatial and temporal scales for multiple, competing reactions. Even in simplified systems, formulation of reactive-transport model descriptions requires parameterization that must aggregate the details of molecular-scale reactions and microbial catalysis to some extent. Investigations of the oxidative dissolution of biogenic U(IV)-oxide (nominally UO2(s)) under anaerobic conditions by either chemical oxidants (nitrate or nitrite) or by Thiobacillus denitrificans, a chemolithoautotrophic bacterium that catalyzes anaerobic, nitrate-dependent U(IV) and Fe(II) oxidation, are used to examine coupled and competing oxidation-reduction processes in flow-through column experiments. Abiotic oxidation of UO2(s) in the presence of nitrate under anaerobic conditions is slow but faster than control experiments of non-oxidative dissolution. Abiotic UO2(s) oxidation by nitrite is significantly faster by several orders of magnitude. In the presence of T. denitrificans and dissolved nitrate, higher rates of dissolved U release were observed compared with abiotic controls, suggesting that T. denitrificans catalyzed the oxidative dissolution of UO2(s) in addition to the abiotic oxidation pathways. X-ray spectroscopic characterization of reaction products indicates solid-associated oxidized U(VI) that is retained in the column. Analysis of local atomic structures shows formation of U-oxo molecular moieties within or on particle surfaces that are similar but not identical to aqueous or sorbed uranyl species, suggesting mostly surface particle oxidation rather than detachment and re-adsorption of uranyl in the column. Reactive transport modeling incorporating thermodynamic solubility, irreversible overall abiotic and biotic kinetic reactions, and uranyl sorption can simulate effluent U concentrations for a small amount of UO2(s) oxidation relative to total mass, but calculations are sensitive to particle surface area.
Remediation Strategies for Redox-Active Elements Using Combined Experimental, Spectroscopic, and Computational Approaches

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Contaminants such as arsenic (As), mercury (Hg), and other redox-active elements pose particular challenges to remediation because of their ability to readily change oxidation state and speciation at surface conditions from coupled microbial-abiotic processes that are spatially and temporally dynamic. A variety of in situ sediment or soil amendment treatments, whether added directly to geomedia or emplaced within barriers or caps, can sequester and stabilize contaminants in place in order to reduce their ability to partition to water or biota, their toxicity, and their potential for transport. Computational approaches such as thermodynamic-kinetic reaction path and reaction transport models capable of simulating biogeochemical, speciation, partitioning, and transport processes are valuable tools for assessing remediation effectiveness when constrained by spectroscopic and experimental investigations of laboratory and field systems. The contrasting chemical behavior and exposure pathways of As and Hg illustrate how remediation approaches using amendments or sediment caps can be optimized by minimizing the concentration of specific chemical species associated with maximum health risk. For As, inorganic arsenite (AsIII(OH)3) is the most toxic form and human exposure is typically through drinking water. Combined field, laboratory, and modeling studies show that sorption or amendment sequestration of arsenate (As(V)) under oxic conditions, or precipitation of solid As sulfides under anaerobic conditions, are most effective for limiting concentrations of dissolved arsenite. For Hg, remediation should target reduction of net methylation of inorganic Hg to methylmercury, which results primarily from bacterial sulfate reduction in anaerobic environments and is the first step in Hg bioaccumulation. Approaches such as sediment chemical amendments or caps can reduce methylation by limiting bioaccessibility of inorganic Hg through solid encapsulation or irreversible sorption, reducing the total concentration of dissolved sulfide species, buffering system oxidation potential above sulfate reduction, and/or buffering pH at circumneutral or above.

Biogenic Influence on Sea-Spray Aerosol and its Impacts


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Marine aerosol, whether primary or secondary, comprises both inorganic and biogenic organic components. Although primary sea-spray mass is dominated by super-micron sea-salt, the sub-micron sizes dominate the sea-spray number concentration leading to important contributions to both direct and indirect radiative effects [1,2]. The relative contributions of sea-salt and primary organic matter to sub-micron sea-spray has been shown to be influenced by biogenic productivity in oceanic waters, with the organic mass fraction ranging from 10% under low biological activity, to 90% under high activity [3, 4]. The organic enrichment reduces the spray’s hygroscopicity [4]; however, there is a dual-state effect leading to hygroscopicity flipping between a high hygroscopicity to low hygroscopicity as the organic matter volume fraction exceeds ~50%. The effect leads to a ~3-fold reduction in scattering enhancement as a function of increasing relative humidity and potentially a reduction in the radiative impact of sea-spray from ~6.5 Wm⁻² to ~1 Wm⁻² under wind speeds of 20 m s⁻¹.

Acknowledgments

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Effects of subduction-related melt extraction on Iapetus Ocean mantle

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Ophiolites enable assessment of the causes and length-scales of mantle compositional heterogeneity because field-based observations can be coupled with geochemical investigations of upper mantle lithologies resolved relative to the petrological Moho. The ~497 Ma Leka Ophiolite (Norway) comprises a section of early-Palaeozoic (Iapetus) oceanic lithosphere with well-exposed mantle and lower crustal sections and remarkably low degrees of serpentinisation (~20%). The Leka upper mantle section is heterogeneous at the cm- to m-scales, manifested by abundant dunite lenses and sheets in harzburgitic host-rock, especially within ~500 m below the Moho. Abundant chromitite (Cr-spinel) and pyroxenite lenses and layers also occur in the uppermost 200-300 m of the mantle section.

The array of mantle lithologies on Leka is considered to have developed during fluid-assisted melt extraction in a supra-subduction zone (SSZ), offering an opportunity to interrogate the nature of Os isotope and HSE abundance heterogeneities developed in such rocks and surrounding metasedimentary units. Initial results show that the Os isotope compositions of the Leka peridotites are quite consistent, with a range of 187Os/188Os of ~1.57 to ~4.43, and Os concentrations ranging from 1-24.8 ng g^(-1) Os, for eleven harzburgites and dunites. Given the similarity between Leka peridotites and estimates of Os isotopic composition and HSE abundances in the oceanic mantle (e.g., abyssal peridotites), we see scant evidence for modification of these elements by SSZ fluid or melt-rock interactions. Comparison of the Leka data with mantle peridotite data from (~492 Ma) Iapetus ophiolite exposed on the Shetland Islands (Scotland) [1] implies that on ocean-basin scales, SSZ fluid/melt interactions may only play a limited role in processing the HSE in already strongly depleted mantle.


Earth’s Hadean crust: Insights from the Nuvvuagittuq Greenstone belt

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The Hadean Eon is still poorly understood due to the scarcity of preserved samples. Most of what we know of early crustal evolution comes from the Hadean Jack Hills detrital zircons. Despite the fact that their host rock has been destroyed, the isotopic composition of these zircons points to a basaltic protocrust reworked to form multiple generations of TTG-like crust. With a minimum age of ~3.8 Ga, the Nuvvuagittuq Greenstone Belt (NGB), represents an ideal terrain to investigate early Earth’s crustal evolution. Rocks from the NGB show considerable variability in 142Nd/144Nd (μ=8 to -18) that can only be produced during the Hadean. The correlation observed between the 142Nd/144Nd and the Sm/Nd ratios of the dominant mafic lithology called the Ujaraaluk unit is consistent with their formation between 4.3 and 4.4 Ga. This age, however, has been challenged because the oldest U-Pb ages on zircons from the NGB felsic rocks are ~3.8 Ga. An alternative model suggests mixing of mantle-derived melts in the Eoarchean with some hypothesized reservoir enriched in incompatible elements during the Hadean to produce the 142Nd deficits of the NGB rocks. This conclusion, however, is not supported by our latest 176Lu-176Hf/142Nd data. Here we present a summary of the geology and geochronology of the NGB and discuss the alternative models of Eoarchean or Hadean age for the belt. We used long-lived and closed Nd isotopic systems (147Sm-143Nd, 176Lu-176Hf for all NGB lithologies including mafic and felsic rocks as well as combined Pb-Hf in zircons to understand the evolution of the NGB and the formation of Earth’s early crust.

Our data suggest that the protolith of the Ujaraaluk unit includes both tholeiitic and calc-alkaline mafic volcanic rocks originally erupted in the Hadean. Reworking of this basaltic precursor over several hundred million years in the Eoarchean produced TTG-type magmatism. If the Ujaraaluk unit is interpreted as Eoarchean, then one must hypothesize the existence of a Hadean enriched component that has identical compositional and isotopic characteristics to the Ujaraaluk as the source of the low 142Nd in both some Ujaraaluk and the NGB TTG suite. We suggest instead that the Ujaraaluk unit is a Hadean mafic protocrust and may therefore represent the first crust to stabilize after the moon-forming impact and be the closest analogue to the primordial crustal source of the Hadean Jack Hills zircons.

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What does Hadean mantle mixing tell us about Hadean geodynamics?

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A hot Hadean mantle is suggested from high internal heat production, high rates of impact bombardment, and significant primordial heat from accretion. Consequently, extremely high internal temperatures argue for low internal viscosities, and extremely vigorous mantle convection. Mixing in such high-Rayleigh number convective environment should have efficiently remixed or erased chemically heterogeneous mantle anomalies on timescales of less than 100Myr.

However, platinum group elements concentrations in Archaean komatiites, purported due to the later veneer of meteoritic addition on the Earth, only achieve current levels at 2.7Ga – indicating a time lag of almost 1-2Gyr in mixing this material thoroughly in the mantle. ¹⁴²Nd and ¹⁸²W isotope studies also indicate that heterogeneous mantle domains survived, without mixing, for over 2Gyr – at odds with mixing rates expected.

Here we suggest the surface tectonic regime may have significantly retarded mixing efficiency in the Hadean. A number of lines of evidence suggest episodic resurfacing in the Archaean, and extrapolating back to Hadean times implies the Hadean was characterized by long periods of tectonic quiescence (albeit violently volcanic). We explore mixing times in 3D spherical-cap models of mantle convection, which incorporate vertically stratified and temperature-dependent viscosities. We show that mixing in stagnant lid regimes can be over an order of magnitude less efficient than mobile lid viscosities. We show that mixing in stagnant lid regimes can be over an order of magnitude less efficient than mobile lid mixing, and for plausible Rayleigh numbers and internal heat production, the lag in Hadean convective recycling can be explained. This explanation not only explains the long-lived ¹⁴²Nd and ¹⁸²W anomalies, but also 1) posits an explanation for the delay between accretion of the late veneer – between 4.5-3.8Ga on a stagnant surface – and its fully mixed signature apparent in elevated PGEs in 2.7Ga komatiites, and 2) provides an explanation for the 400Myrs of immobility of the mafic protolith from which the Jack Hill zircons were sourced, and 3) retards early heat loss from the mantle, providing a solution to the “Archaean thermal catastrophe” of parameterized Earth evolution models.

The effects of silicate melt composition and sulfur on the solubilities of PGEs in silicate melts

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Experimental studies of PGE solubilities at conditions directly relevant to natural basaltic melts are difficult because the low solubilities are often masked by variable amounts of micronuggets suspended in the melts. Experiments in simple haplobasaltic melts appear to establish that solubilities at low pressures are less than ~1 ng g⁻¹ at typical terrestrial oxygen fugacities and temperatures, raising questions as to how PGEs are transported from the mantle and concentrated into economic ore deposits. The applicability of the simple system experiments is sometimes queried because, it is claimed, missing ingredients like Fe or S might enhance solubilities. To address this issue directly, the effect of melt composition on Ir and Pd solubilities has been determined at ambient pressure. Samples were equilibrated in a 1-atm. gas-mixing furnace using Ir and Pd metal loops, quenched to glasses and analysed by laser ICP-MS (detection limits < 1 ng g⁻¹), with EMPA for major elements and sulfur. The compositional dependence was studied first at high temperatures (1500°C for Ir and 1400°C for Pd), which reduces the micronugget problem, and compositions least affected by micronuggets were then selected to measure the effects of T and fO₂. For Ir, ~ 40 melt compositions in CaO-MgO-Al₂O₃-SiO₂±FeO±Fe₂O₃±Na₂O±TiO₂ were investigated. The results show that Ir dissolves only as Ir⁺⁺ over the experimentally accessible range of fO₂, and solubilities are simply related to the melt composition through its optical basicity. The effects of FeO and Fe₂O₃ are small but individually resolvable: fO₂-corrected solubility decreases as Fe₂O₃ replaces FeO. High Fe or Ti suppresses micronuggets. As regards sulfur, Ir solubility is too low for any effect to be seen at the fO₂s needed to achieve measurable S²⁻ in the melt in 1-atm experiments. Pd dissolves as Pd⁺⁺ with some Pd⁺⁺ at higher fO₂, in agreement with literature results. The effect of melt composition on Pd solubility is much less than for Ir, and is not related to any simple compositional variable. To investigate the effect of S quantitatively, experiments on the solubility of Ru (as Ru⁺⁺), which is ~ 50 times more soluble at a given fO₂ than Ir, were undertaken using a high Fe-Ti picritic composition at 1500°C to eliminate micronuggets, in olivine capsules. Only a small effect was observed despite ~1000 µg g⁻¹ S²⁻ in the melt.
Archean lithospheric mantle: The fount of all ores?

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Magma-related ore systems form economic deposits that underpin our human civilisation. The magmas related to metallic element redistribution derive from the asthenosphere, then traverse and interact to varying degrees with the subcontinental lithospheric mantle (SCLM). Convergent geochronology datasets of Hf isotopic model ages for zircons and Re-Os model ages for mantle sulfides, reinforced by other geochemical and tectonic criteria, indicate that over 70% of the SCLM and its overlying crust (now mostly lower crust) formed at about 3.5 Ga, probably in a global overturn event that marked a change in Earth’s fundamental geodynamic behaviour. This primitive SCLM, the roots of the Archean cratons, was geochemically highly depleted, and subsequently played a major role in crustal metallogeny for many ore types.

Firstly, the high degree of buoyancy of this ancient SCLM relative to the asthenosphere, due to the Mg-rich and Fe-poor composition, results in persistence today of low-density, rheologically coherent Archean domains (including relict crustal metallogeny for many ore types. Secondly, the enduring (and volumetrically dominating) Archean lithospheric mantle domains represent a reservoir for metasomatic enrichment over their 3.5 billion year history, creating a potentially metallogenically fertile mantle material. Thirdly, the formation of Archean cratons provide an architectural lithospheric mantle-source for ore-forming elements depending on the geodynamic evolutionary stage. Fourthly, if this first stabilisation of lithospheric mantle at 3.5 Ga signalled the end of an overturn regime (either uniquely, or intermittent with subduction), then long-lived tectonic regimes conduces to mineralising systems (e.g. back-arc basins, passive margins, crustal boundaries) became available.


P-T modeling reveals juxtaposition of units within the Gruf Complex (Central Alps) during orogenesis.

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Equilibrium assemblage diagrams calculated with Theriaek-Domino are used to constrain peak P–T conditions of sapphire granulites and migmatitic paragneisses. Residual orthopyroxene + garnet + sapphire + sillimanite granulites record peak conditions of 900–960°C at 8–10 kbar. Subsequent UHT decompression to <8 kbar produced cordierite coronae around peak minerals. Complex compositional zoning patterns in garnet porphyroblasts suggest no diffusional equilibration at peak conditions and thus a short-lived UHT event. Muscovite-bearing and muscovite-free paragneisses reached peak conditions of 650–700°C and 700–750°C, respectively, at ≈7.5 kbar. The paragneisses contain no evidence for UHT metamorphism. The different peak conditions suggest that peak metamorphism of the granulites and paragneisses occurred at different crustal levels. The granulites and associated amphibolites were subsequently juxtaposed against the paragneisses and associated orthogneisses along mylonitic shear zones.

Ages of zircon rims in granulites suggest they underwent UHT metamorphism at ≈32.7±0.5 Ma (Liati & Gebauer, 2003, MPM). Variably deformed aplite and pegmatite dikes crosscut all other rock types and are deformed within the mylonitic contacts between the granulite–charnockite and paragneiss–orthogneiss units (Galli, 2010, PhD thesis, ETH Zürich). The dikes crystallized at ≈30 Ma, suggesting juxtaposition occurred between 33 and 30 Ma, coeval with crystallization of the Bergell tonalite–granodiorite. By c.24 Ma, the granulites and thus the entire Gruf Complex cooled below the U-Pb closure temperature of rutile (Oalmann et al., 2011, Goldschmidt abstract), coinciding with crystallization of the Novate S-type leucogranite and the latest, undeformed dikes.

UHT metamorphism coincides with the transition from (U)HP to Barrovian metamorphism in the Central Alps. Therefore, heat for UHT metamorphism likely resulted from asthenospheric upwelling after slab breakoff. Exhumation and juxtaposition of units within the Gruf Complex was likely related to the emplacement of the Bergell intrusion.
Isotope effect in the formation of solid water by surface reactions at 10 K

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D/H ratio of water in molecular clouds (MCs) is often 2-3 orders of magnitude higher than that of terrestrial ocean water (D/H~1.56×10^{-4}). Such a significant deuterium enrichment often observed not only for water but also organic compounds like formaldehyde and methanol in MCs [1] cannot be explained by the gas-phase fractionation only. It is at present widely recognized that grain-surface reactions are crucial for the formation and deuterium enrichment of those molecules.

Among various reactions proposed, the reaction OH+H_{2}→H_{2}O+H is considered to have a significant contribution (>70%) to H_{2}O formation in dense MCs [2] where the typical temperature is ~10 K. It is therefore reasonable to assume that deuterated water like HDO could also be formed by the similar surface reactions such as OH+D_{2}→HDO+D and OD+H_{2}→HDO+H. In the present study, we performed laboratory experiments on the formation of water (H_{2}O, HDO, or D_{2}O) by reactions of OH/OD with H_{2}, HD, or D_{2} on a solid substrate at 10 K.

Experiments were performed under ultra-high vacuum conditions (~10^{-8} Pa). OH or OD radicals were produced by the dissociation of H_{2}O or D_{2}O in microwave-induced plasma and cooled to 100 K. Each radical was codeposited with H_{2}, HD, or D_{2} on a substrate at 10 K.

We found that all reactions studied occur on the substrate at 10 K. However, the reaction efficiency was clearly different between H- and D-atom abstraction reactions from H_{2}, HD, or D_{2}. The former reactions (e.g. OH+H_{2}→H_{2}O+H) were about 10 times more efficient than the latter (e.g. OH+D_{2}→HDO+D). The difference in efficiency is derived from the different effective masses of reactions. The efficiency does not depend on the kind of hydroxyls (OH or OD) but only on that of atoms abstracted.

The present study suggests that one of the important factor to control the D/H ratio of water in MCs is OD/OH ratio. If OD and OH were produced by D- and H-addition to O atoms on grains, respectively, atomic D/H ratio in MCs would be crucial for constraining the D/H of water in MCs.


Distribution of iron (II) in the Northwestern Pacific

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Iron is an essential micronutrient for marine phytoplankton and its availability affects marine primary production in the ocean. Among iron species in seawater, Fe(II) is readily bioavailable form for phytoplankton, but its distribution is not clearly revealed. In this study, the distribution of Fe(II) along the 160° E line in the Northwestern Pacific was investigated. Seawater samples were collected during the R/V Hakuo-maru cruise (6 July – 3 August, 2012) with acid cleaned X-Type Niskin samplers deployed onto a CTD-CMS. Dissolved Fe(II) was determined quickly after sampling onboard the ship with luminol chemiluminescence method [1].

We observed the Fe(II) maximum (6 – 54 pM) in the oxygen minimum zone (OMZ) commonly. Dissolved oxygen concentrations were 14 - 58 μM in the OMZ, where in-situ Fe(III) reduction did not occur. During the remineralization process of biogenic particles, Fe(II) was probably released and/or produced in the reducing conditions within the settling particles [2].

Ions, vapors and/or nanoparticles penetrating volcanic edifices?

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A top-sealed plastic tube with a diameter of ca. 15 cm had been buried ca. 70 cm deep vertically at the base of La Fossa volcano, Vulcano island, Italy, next to the front of the obsidian flow. The tube had been filled with layered rock and quartz wool to condense vapors emanating from the soil. At ca. 75 cm below the surface the sample had been exposed to vapors from Sept. 2005 to April 2006. The leached sample had not been in touch with the ground. 2 other glass wool cushions (ca. 10 cm thick, uncompacted) had been underneath to minimize capillary effects. A rock wool layer not touching (ca. 10 cm thick, uncompacted) had been in touch with the ground. 2 other glass wool cushions from Sept. 2005 to April 2006. The leached sample had not been in touch with the ground. 2 other glass wool cushions (ca. 10 cm thick, uncompacted) had been underneath to minimize capillary effects. A rock wool layer not touching ground revealed nucleated sylvite (KCl ~10 µm in size) and barite (BaSO4 ~5-10 µm in size) crystals by SEM/EDS in its ground revealed nucleated sylvite (KCl ~10 µm in size) and barite (BaSO4 ~5-10 µm in size) crystals by SEM/EDS in its basal portion. Other very small (< 2 µm) particles were observed on the rock wool fibers but we could not identify them because they were suddenly volatilized by the electron beam. The bright appearance in backscattered images suggests that these particles may be metal compounds. The nucleation of sylvite and barite documents the presence of ions. Leaching of the quartz wool at room temperature with deionized H2O and ICP-MS analysis documented 4 groups of elements: 1. positive signal: Mg, K, Ca, Cr, Mn, Ni, (Ba); low to moderate volatility at magmatic conditions. 2. unclear signal: Al, Si, P, Fe; low volatility at magmatic conditions. 3. no signal: V, As, Se, Mo, Co, As, Se, Mo, V are considered to be highly volatile, Co got a low volatility. 4. positive signal: Cu, Zn, Cd, Sn, Pb, W; high volatility at magmatic conditions. Leaching with nitric acid documented also V and Fe, and produced higher values for all elements, except K and Sn. This experiment documents for the first time an unknown element transport by vapors/gases through a volcanic edifice interacting with hydrothermal and magmatic gases. More information can be found at http://www.iugg2007perugia.it/webbook/

Volatiles in arrojadite: combining single-crystal XRD and FTIR microspectroscopy

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Arrojadites are complex phosphates typically found in granitic pegmatites or hydrothermal veins, although their occurrence in metamorphic rocks suggests wider conditions of formation. Re-examination by EMP, LA-ICP-MS and single-crystal XRD analysis of a set of samples from various occurrences lead to revise the structure, the formula and the nomenclature of the group [1,2]. The correct structural model for arrojadite implies three OH-groups: two of these (W1 and W2) have similar local environment (they bridge three octahedra), crystallographic orientation and hydrogen-bond system. W3 is connected with the apical oxygen of a newly defined tetrahedron in the structure, and is involved in a bifurcated hydrogen bridge with surrounding oxygen atoms. Raman spectra reported in [1] show two higher-frequency, intense and convoluted bands which were assigned to specific local environments of W1 and W2; an additional low-frequency, broad and weak feature in the spectra could not be assigned with certainty. We report in this work on a FTIR study of various samples studied in [1,2]. Chemical zoning of the volatile components was checked by FTIR imaging using an FPA detector fitted on a Bruker Hyperion 3000 microscope. In contrast with the Raman spectra, the FTIR patterns show a very intense and broad absorption extending from 3500 to 2900 cm⁻¹. Single-crystal XRD has shown that F is ordered at the W1 site, and this generates a significant modification of the FTIR pattern, as observed on holotype fluoro-arrojadite-(BaFe) from Sidi Bou Kricha (Morocco).

The FTIR spectrum of holotype arrojadite-(KNa) from Rapid Creek shows also an intense doublet at 3190-3087 cm⁻¹ which can be assigned to NH4⁺ groups, as later confirmed by EMPA. The orientation of the absorber (i.e. the O-H bond) with respect to the crystallographic axis can be determined from polarized-light measurements along the principal optical direction [4]. In all the samples, no evidence of molecular water is present in the NIR 4000-6000 cm⁻¹ region.

Rare Earth Elements in the sediments of Lake Baikal

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Lake Baikal is the deepest and oldest lake on Earth. However, the biogeochemical cycling of major and trace elements in this oligotrophic lake and its watershed have received relatively little scientific attention. The Rare Earth Elements (REEs), in particular, have gained importance as powerful tracers of chemical processes on the Earth’s surface as they form a relatively coherent group of elements with, nonetheless, sensible differences among them. Cerium (Ce) and Europium (Eu), for example, are the only REEs which exhibit redox-sensitivity. The present study offers an overview over the REE chemistry in Lake Baikal and its catchment area and more specifically their distribution in five short sediment cores distributed across the Lake at different depths whereby we analysed and discussed normalised REE patterns and their consequential Ce, Eu and gadolinium (Gd) anomalies. We found that, while particulate REE concentrations are mainly influenced by processes above or near the surface of Lake Baikal, such as the development of a widespread negative Ce anomaly, early diagenetic chemical activity is best reflected in the dissolved fraction of the REEs, where their complexation with inorganic and organic ligands plays an important role in addition to adsorption onto metal oxides and clay minerals. A further extraordinary feature found within the lake’s sediments are highly positive Eu anomalies, which are otherwise rare in sedimentary systems, in particular within Fe- and Mn-oxide accumulations buried within the reducing part of the sediment. Eu anomalies correlate with elevated barium (Ba) contents which are likely associated with phosphates and/or manganese oxides and we argue that Eu substitutes for Ba. Furthermore, while the Ce and Eu anomalies are formed within the watershed and the sediment respectively, the omnipresence of positive Gd anomalies in the sediment and the pore waters can be traced back to the atmospheric input into the lake.

Uptake of radiocesium by crops from soils contaminated by the Fukushima Accident

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Cs-137 (T1/2; 30.1 y) and Cs-134 (T1/2; 2.06 y) were released by the accident of Fukushima Daiichi NPP and agricultural fields in Fukushima prefecture were widely contaminated. More than 2 years after the accident, some crops exceed the guideline for radiocesium (100 Bq/kg) and the mechanism of higher uptake is poorly understood. We investigated radiocesium and stable element concentrations in rice plants and komatsuna (a leafy vegetable) grown in soils which were collected from the contaminated fields in Fukushima Prefecture. We discuss mechanisms of radiocesium transfer with special reference to the soil characteristics in this study.

Cultivation experiments using soil that was contaminated with radiocesium were carried out in Fukushima Agricultural Technology Centre and the radiocesium concentrations of both soil and plant samples were determined by a Ge-detector at Gakushuin University. The plants were cultivated in Wagner pots (3 L) in a greenhouse.

As a result, the highest values for transfer coefficient were observed in crops grown in brown forest soils, while the plants cultivated in gray lowland soil showed the lowest values. In order to compare soils with different radiocesium levels, we collected them from the top layer with high radiocesium concentrations (upper 5 cm) and from the underlying soil with lower concentrations (5–15 cm). We cultivated komatsuna and found that the transfer coefficients of plants grown in the underlying soils are greater than those of komatsuna planted in the surface soils. This might be related to the speciation of radiocesium in the soils. Deeper layers may have more labile, plant-available radiocesium, while less labile particulate-bound radiocesium from the accident may be more common in the surface soils.

Additionally, we have also carried out stable element analysis (including Cs) in crops and soil extracts to examine whether there is any correlation between the transfer factor of radiocesium and that of stable elements.

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Assessment of Groundwater Quality in some parts of Southwestern Nigeria

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One hundred and twenty samples from groundwater were collected at Ago Iwoye, Oru and Ijebu Igbo, Southwestern Nigeria. The purpose was to establish preliminary baselines for these constituents in the ground water of the study area and also to determine the quality. The analysis of trace elements and cations in water were carried out using inductively coupled plasma optical emission spectrometry (ICP-OES at Acme, Ontario Canada). Concentrations of 34 elements which include trace and major elements such as Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Sb, Se, Si, Te, Ti, U, V, W and Zn were determined. Trace elements like Si, Bi and Ti were below detection level of 0.05 ppb, 0.05 ppb and 10 ppb respectively for all the samples. As, Be, Cd, Cr, Cu, Mn, Se and Zn were below Maximum Contamination Level (MCL) of EPA 2012 for all the samples. Al, Br, Fe, Mn, Ni, Pb, Sb were above the standard and generally pose health or environmental hazard for most of the samples with the following ranges <1-2686 ppb, 5.48-2199.35 ppb, <10-22450 ppb, <0.05-52.8 ppb and 0.09-11.64 ppb respectively. The pollution index among all sites varied from 0.075 to 6.26 and exceeded the acute and chronic effect levels proposed by the United States Environmental Protection Agency in 2007.

Production of S-MIF Signatures during Photochemistry of Biogenic Volatile Sulfur Compounds: A Potential Marker for Marine Stratospheric Sulfur Aerosol Layer

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Sulfur mass-independent fractionation (S-MIF) has been reported for UV-photochemistry SO2 and CS2 but not for OCS and H2S. These experimental observations have been linked to S-MIF signatures observed in sedimentary sulfides and sulfates of Archean and Early Palaeoproterozoic age, and have been used as evidence for a low-pO2 atmosphere on the Early Earth. Although biogenic methylated sulfur compounds is important in atmospheric sulfur cycles today, multiple-S isotope effects of photochemistry of dimethylsulfide (DMS), dimethyldisulfide (DMDS), dimethyltrisulfide (DMTS), and episulfides (e.g., ethylene sulfide (ES)) have not been reported. Characterizing multiple sulfur isotope effects during photochemistry of these organic sulfur compounds may be used to study the fate for marine biogenic sulfur, particularly DMS photochemistry, which is the most abundant biogenic sulfur gas in our present atmosphere.

We will report that broadband UV-photolysis of DMS, DMDS, and ES using a Xenon-Arc lamp produced S-MIF signals with magnitudes of $\Delta^{33}S$ up to +2.9 ‰ and $\Delta^{36}S$ up to +0.9 ‰ for the solid aerosol sulfur products with significant changes in $\delta^{34}S$ fractionations up to +7.1‰. UV-photolysis experiments with water vapor produced relatively small to no S-MIF signals in some of their oxidation products (e.g., sulfate and sulfonic), which may likely result from HOx oxidation reactions via direct or indirect photodissociation reactions of; O$_2$ + O + O$_2$ and H$_2$O + O → 2HO. These biogenic gases undergo a rapid oxidation when emitted to the present day atmosphere, and its oxidation products can be transferred above the tropopause and contribute to stratospheric cloud-condensation nuclei (CCN). Our results suggest that the production of S-MIF could be potentially possible even in today’s atmosphere containing biogenic sulfur gases. We hypothesize that these S-MIF signals can be used as a marker to identify the source of sulfur aerosols where biogenic sulfur constituents affect radiative forces.

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What can spectral properties of SNCs and Martian surface tell us about crust-mantle system evolution?

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The SNC meteorites are the only samples of Mars available for analysis on Earth, providing unique insights into the formation and evolution of the Martian crust-mantle system. However, the absence of identified source regions and the debate surrounding the age of shergottites limits exploitation of the mineralogical and geochemical information provided by these rocks. With this in mind, a comparison between the near-infrared (NIR) spectral properties of the SNCs and spectra of the Martian surface from the NIR imaging spectrometer OMEGA/MEx has been made. We show that shergottite spectra are comparable to those of early Amazonian [1]. This result is largely controlled by the fact that olivine is mainly associated with three different geological settings [2]: (1) ejecta around the Hellas basin with an intermediate to forsteritic composition suggesting a Mg# >50 for the excavated upper mantle, (2) large impacts and crustal outcrops that argue for olivine in deeper sections of the crust in the form of cumulates or alternatively in a global layer of older (early Noachian) rocks, (3) early Hesperian lava flows throughout the Martian surface suggesting a planetary event of olivine-enriched fissural volcanism. In contrast, olivine is not detected in Noachian terrains that formed the major part of the southern highlands. This fact could be related to an evolution in magma composition or in the degree of olivine fractionation between these two epochs.

These results will be discussed in light of the predictions of petrologic models for the formation and evolution of the Martian crust-mantle system [3,4].


Reversibility of calcium and magnesium isotopic signatures during ambient temperature fluid-carbonate mineral interaction

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The interpretation of mineral isotopic signatures in low temperature fluid-rock systems commonly relies on the assumption that they remained unchanged since their precipitation over geologic time, despite potentially being out of isotopic equilibrium with their co-existing fluids (e.g. the use of carbonate isotopic compositions to deduce paleo temperatures). Similarly, fluid compositions are frequently interpreted assuming that isotopes are conservatively transferred from minerals to fluids as they dissolve.

In an attempt to test such assumptions, we have dissolved both calcite and hydromagnesite (Mg5(CO3)4(OH)2*4H2O) in closed-system reactors from far to near to equilibrium conditions in aqueous NaHCO3/Na2CO3 solutions at constant pH from 6.5 to 9. Ca and Mg were strongly fractionated during the stoichiometric dissolution of these minerals; in each case the fluid is significantly isotopically heavier than the dissolving mineral. For example, calcite dissolution at pH ~6.8 yielded a fluid phase that was ~0.65‰ heavier than the dissolving mineral during the 3 days required to attain equilibrium. Correspondingly, the calcium in the solid phase became ~0.14‰ higher during this experiment. Isotope fractionation during stoichiometric dissolution is interpreted to stem from the two way transfer of material to and from the mineral as elemental equilibrium was approached, consistent with the concept of microreversibility. Preliminary mass balance calculations suggest that more than 20% of the Ca contained in the calcite present in this experiment must have passed through the fluid phase to attain this degree of fractionation. Similarly, hydromagnesite dissolution at ~pH 8.4 yielded a fluid phase that was ~0.3‰ heavier than the dissolving mineral during the 3 days required to attain equilibrium. In some cases, the isotopic composition of the fluid continues to evolve after the mineral attained elemental equilibrium. These observations clearly contravene the concept of conservative isotopic mass transfer during mineral dissolution and questions the degree to which mineral isotopic signatures can be preserved in low temperature systems.
Using coupled Fe-Mg chemical and isotopic diffusion profiles to model magma residence times of crystals

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Recent studies have shown that chemical diffusion at magmatic temperatures generates Fe and Mg isotope fractionation in olivine that exceeds potential equilibrium isotope fractionation by an order of magnitude [1,2]. Accordingly, diffusion-generated Fe-Mg chemical zoning in olivine should be coupled with Fe-Mg isotopic zoning. In this case, magma residence times of crystals can be derived by adequate modeling of both, chemical and isotopic zoning.

This approach has been tested on olivine grains in basaltic rocks from the Massif Central volcanic region (France). Large, chemically zoned olivines were analyzed by femtosecond laser ablation MC-ICP-MS. With this technique an external precision of ±0.10‰ (2 SD, based on replicate analyses of glass standards) can usually be achieved for both δ56Fe and δ26Mg.

Several olivines show significant Fe-Mg isotopic zoning (of up to 1.5% for δ56Fe and up to 0.8% for δ26Mg) that is coupled with the chemical zoning (i.e. Mg#. Furthermore, the zoning profiles of δ26Mg and δ56Fe are negatively correlated. This strongly indicates that the observed zoning was generated by diffusion of Fe into and Mg out of the olivine during magma evolution (e.g. [3]). Simplified and independent modeling of Fe- and Mg- chemical and isotopic zoning was used to estimate the duration of Fe-Mg inter-diffusion between crystal and melt, which may reflect the residence time in a magma chamber before eruption [4]. Our results point to minimum magma residence times between 0.5 and 10 years, which is similar to the short timescales determined by diffusion modeling of chemical gradients in olivines hosted in basaltic lava flows from Mt. Etna [5].

A major focus of our project is to apply our developed technique to olivine crystals in MORBs to improve our knowledge on magma evolution at mid-ocean ridge settings. Olivines from the Mid-Atlantic Ridge and the Costa Rica Rift show both normal zoning and reverse zoning of forsterite (up to 4 mole percent). Fe-Mg isotopic profiles will be determined to prove whether the chemical zoning was generated by diffusion and thus provides information on magma residence times of these olivines.

Biominalization of jarosite by
Purpureocillium lilacinum, an
acidophilic fungi isolated from Río
Tinto
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Río Tinto (Huelva, Southwestern Spain) is an extreme
environment with a remarkably constant acidic pH and a high
concentration of heavy metals, conditions generated by the
metabolic activity of chemolithotrophic microorganisms
thriving in the rich complex of the Iberian Pyrite Belt (IPB).

In this study, we report the specific biominalization of
(hydronium)-jarosite, an iron sulfate mineral that appears in
abundance on Río Tinto banks by an acidic fungal isolate,
*Purpureocillium lilacinum*. Different fungal species were
isolated from Río Tinto; characterized, cultured and tested for
their ability to promote the formation of jarosite. Of the 10
strains tested, only *P. lilacinum* was able to produce jarosite.
The biominal was characterized by X-Ray Diffraction
(XRD) and its formation was observed with high-resolution
transmission electron microscopy (TEM) and scanning
electron microscopy (SEM) coupled to Energy-dispersive X-
ray spectroscopy (EDX) microanalysis.

Jarosite began to nucleate on the fungal cell wall, even on
dead cells (although with much less efficiency). Also
extracellular polymeric substances (EPS) released by the
fungus could serve as nucleation sites for this biominalization process. Our model proposes the creation of Fe³⁺/Fe²⁺-rich microdomains in the cell walls of *P. lilacinum*
that induce the supersaturation and precipitation of jarosite.
This change in the proportions of reduced and oxidized iron
species, can be produced by the electrostatic interaction
between soluble ferric iron and the negatively charged groups
of the fungal cell wall, acting as nucleation sites for mineral
precipitation according to previous studies [1].

The occurrence of *P. lilacinum* in an ecosystem with high
concentrations of jarosite strongly suggests that might participate actively in the formation of this mineral in the river
banks.


The biological control on the
atmospheric $pCO_2$ level through
gologic time

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Here we constrain the atmospheric $pCO_2$ levels during the
evolution of the Earth’s biosphere through pre-biotic,
aerobic, pre-plant aerobic, and plant stages based on the
BLAG-type geochemical modeling of $CO_2$ cycling. We have
developed a new set of equations considering: (i) the flux and
fate of $CO_2$ and reduced volcanic gases; (ii) the biological
influence of soil formation; (iii) the cycling of phosphorus-
bearing compounds; (iv) the C/P ratios of kerogen; (v) the
burial efficiency of organic matter in sediments; (vi) the
weathering efficiency of kerogen; (vii) the production
efficiency of biogenic CH4; and (viii) the formation of organic
haze in the atmosphere and the deposition of haze-C in
sediments. Our modeling suggests that the atmospheric $pCO_2$
remained at > 100 PAL during most of the pre-biotic-, aneobic-, and
pre-plant aerobic stages. No additional greenhouse gases (e.g., CH4, H2) were necessary to maintain a
warm Earth under a faint young Sun. A transition of the
biosphere caused a drastic change in the atmospheric
$CO_2$ level: a drop from >1,000 to ~100 PAL due to the
development of an anaerobic world; a rise from ~100 to
~1,000 PAL during the anaerobic to aerobic transition; and a
drop from ~20 to ~2 PAL due to the development of the plant
world. Fluctuations in the soil-forming land area profoundly
affect the climate of the Earth. Continental breakup would
result in a global cooling event, while the formation of
supercontinents would result in global warming.
Ocean-pH evolution and weathering conditions during the Ediacaran: Insights from B, Sr & Li isotopes at the Gaojiashan Section, South China

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The Ediacaran to Cambrian transition was a decisive time in Earth history since substantial changes in ocean-atmosphere interactions, climate, tectonics and bio-geochemical processes catalyzed the advent and radiation of metazoa. In this study, we investigate the boron, strontium and lithium isotope records of the Algal Dolomite, Gaojiashan and Beiwan Members (all Dengying Formation) at the Gaojiashan section in south-western Shaanxi, South China to gain detailed insights into changing ocean-pH and weathering conditions. The 65 m thick carbonate-siliciclastic Gaojiashan Section is located at the north-western margin of the Ediacaran Yangtze-platform. Sedimentary data suggest a near shore shallow water setting that is exceptionally well preserved and only present in this part of the platform. Carbonate sedimentation is influenced by continuous detrital input presumably from a pro- and retrograding delta front.

In the upper part of the Gaojiashan Member, a negative δ13C and δ11B anomaly is unveiled with nadirs down to ~ -7‰ for carbonate carbon and -12‰ for boron, respectively. In total, the excursion comprises a shift of -13‰ for δ13C and -12‰ for δ11B which equals a decrease of ~ 1.5 pH units. At the same time, Sr isotopes display a positive excursion (87Sr/86Sr 0.7085 to 0.7110) indicating a time of enhanced weathering through relative sea-level fall. To further assess the continental silicate weathering flux, Li isotopes have been analysed.

If we accept that those changes in the isotope pattern and ocean geochemistry are of primary origin, it needs to be discussed whether a (temporarily) restricted environment or open-ocean conditions are recorded. In view of the pronounced negative δ13C anomaly it must also be considered that the Precambrian-Cambrian boundary interval is recorded in the uppermost Gaojiashan Member and the overlying sediments already belong to early Cambrian strata.

Determination of 129I by ICP-MS/MS; it’s application to Fukushima soil samples

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The accident at the Fukushima Daiichi nuclear power plant (FDNPP) resulted in a substantial release of radioiodine and radiocesium into the environment. The distribution of radioiodine has been studied. On the other hand, 131I could only be determined within a couple of months, due to its short half-life (8 days), resulting in a lack of data on the deposition of this nuclide. Another iodine isotope, 129I (half-life: 1.57 × 107 y), was released simultaneously with 131I. To reconstruct the early distribution of 131I, 129I has been used as a tracer. The determination of 129I in Fukushima soils is of importance to investigate the distribution of radioiodine released from the FDNPP.

Recent advances in ICP-MS/MS (Agilent 8800) have enabled us to determine the long-lived radionuclide 129I in soil samples. The ICP-MS/MS has an additional quadrupole mass filter, situated in front of the reaction cell, which allows only the analyte mass to enter the cell. Therefore, polyatomic interferences, such as 127I 1H2, generated in the cell, can be reduced. In this study, we measured 129I in samples collected from an orchard in Koriyama-shi (about 60 km from the FDNPP). The measured 129I/121I ratios in the samples by ICP-MS/MS are consistent with the value determined by AMS within the analytical error, suggesting the applicability of this method to measurements of 129I in Fukushima soils. We also examined the depth distributions of radioiodine and radiocesium in the orchard. Sampling was carried out in April 2011 and July 2012. Our results demonstrate that, in April 2011, more than 80% of the radioiodine was distributed in the upper 4 cm of the soil column in the orchard. About one year after the accident, the proportion of the inventory in the upper 4 cm was about 60%, indicating 20% of the radioiodine had transferred to the lower part of the column. On the other hand, no significant change was observed in the depth distribution of radiocesium. This result suggests that it is difficult to use radiocesium as a tracer of 131I released from the FDNPP.

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Influence of depth on soil organic matter characteristics: An ultrahigh resolution mass spectrometry study

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The characterization of soil dissolved organic matter (DOM) is a fundamental challenge given its diversity, chemical complexity, and importance in many vital ecosystem processes. We analyzed podzolic B horizon soil collected at multiple depths from the Bear Brook Watershed in Maine (U.S.A.) to study changes in soil DOM chemical properties with depth using ultrahigh resolution mass spectrometry.

The results show that for the B horizon-derived DOM, the Aromaticity Index (A.I.) decreases with depth, indicating that the more aromatic components of DOM are preferentially being removed either through sorption with surface functional groups and/or microbial processes. Also with increasing B horizon depth, the van Krevelen diagram classified protein-like DOM components (those that are aliphatic) increase in relative content. Increases in these chemical classifications have been linked to microbial processes.

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>A.I. &gt; 0.5</th>
<th>A.I. &gt; 0.67</th>
<th>VKD Proteins</th>
<th>VKD Lipids</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 0-5 cm</td>
<td>19.5</td>
<td>5.3</td>
<td>24.0</td>
<td>0.2</td>
</tr>
<tr>
<td>B 5-10 cm</td>
<td>14.3</td>
<td>2.5</td>
<td>26.0</td>
<td>0.4</td>
</tr>
<tr>
<td>B 10-15 cm</td>
<td>11.2</td>
<td>1.2</td>
<td>26.9</td>
<td>0.7</td>
</tr>
<tr>
<td>B 15-20 cm</td>
<td>11.2</td>
<td>1.8</td>
<td>29.0</td>
<td>0.6</td>
</tr>
<tr>
<td>B 20-25 cm</td>
<td>9.1</td>
<td>0.6</td>
<td>30.9</td>
<td>0.8</td>
</tr>
<tr>
<td>B 25-50 cm</td>
<td>9.2</td>
<td>0.7</td>
<td>31.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 1: Influence of soil depth on DOM chemical properties of soils from a reference hardwood stand.

The results are consistent with the hypothesis of Kaiser and Kalbitz [1], who suggested that near-surface DOM is more related to plant-derived molecules, while DOM at depth has a greater content of microbially-derived molecules.


Autoradiography analysis on local area distribution of radiocesium in trees from FDNPP

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The nuclear accident at the Fukushima Daiichi Nuclear Power Plant (FDNPP) occurred as a consequence of the massive earthquake and associated tsunami that struck the Tohoku and north Kanto regions of Japan on 11 March 2011. A series of hydrogen explosion was occurred from 13 March to 15 March at the units 1, 2, and 3. The release rate of $^{137}$Cs on 15 March is estimated between $10^{12}$ and $10^{15}$ Bq/h [1]. This fallout radioactive Cs were dispersed from FDNPP to ocean [1,2] and land [1]. Some of the released radiocesium was deposited on the area located north-west direction from FDNPP. We should elucidate the migration behavior of radiocesium in environments.

Local area distribution and relocation of radiocesium in trees has been studied by measuring its spatial distribution on/in trees using autoradiography analysis. The samples of trees were collected on the places located between 4 and 55 km from FDNPP at approximately 2, 8, 20, and 22 months after the accident. The autoradiography analyses of Cryptomeria japonica, Torreya nucifera, and Thujsopsis dolabrata var. hondae collected on approximately 2 and 8 months after the accident showed that radiocesium was mainly distributed as like spots on the branches and leaves of the trees emerged before the accident, and was little detected in new branch and leaves emerged after the accident. On the contrary, radiocesium was detected at the outermost tip of branches in the trees collected after 20 months of the accident. Morus alba collected after 22 months contained radiocesium in and outside of the stem, even though no radiocesium was detected in the root, strongly suggesting that some radioacesium was translocated from the outside stem to inside. These results indicate that distribution of radiocesium deposited on/in the trees has been gradually changed with time in the scale of the year.

Leakage behavior of gases to bottom water through sediment layers with gas-hydrate stable conditions

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The water under the main thermocline in the Japan Sea is a single water mass referred to as the Japan Sea Proper Water (JSPW). It can be defined as having temperature below 2.0°C, salinity above 34.0. It is known that wintertime air-sea interaction in the Japan Sea, enhanced by outbreaks of dry and cold air masses from the Eurasian continent, generates the JSPS characteristic water mass through deep convection.

Below 10 °C, carbon dioxide hydrate is stable over the pressure of 4.4 MPa. In the Japanese archipelago side of the Japan Sea basin, the area with a water depth from 200 m to 1000 m is several thousand square kilometers, which is attractive for the CO2 storage in the sub-seabed geological formations with at least 1011 tons of CO2 storage capacity; in the process of upward migration, the leaked CO2 would have much chance of hydrate formation reaction in situ.

While the most famous natural analog is the CO2 seepage in mid-Okinawa Trough backarc basin found by Sakai et al. [1], the recently-found seafloor methane hydrate outcrops occurring on the top of the CH4 plume in the sediment layers [2] also provides an insight into the leakage mechanism for liquid CO2.

Gaseous CH4 plume will be self-sustaining by its dry-out effect in the sediment and be hence developing its size as large as of several hundred meters in diameter [2], which would enhance the mixing of gas with the ambient water to make hydrate crystal growing effectively. The key is the low density of CH4 hydrate (less than 1.0) that brings about buoyant behavior of the hydrate solid out of the bottom sediment into the overlying water column in the long run. On the contrary, liquid CO2 might not make a gaseous plume due to its higher solubility in water and small upward migration driving force. The upward migration path could be like a dispersed mesh network in shape, partly due to the increased density of the interstitial water in contact with liquid CO2 (i.e., partial molar volume of CO2 gas in aqueous solution is ca. 32cm³/mol). Self sealing of the leaked CO2 in situ is probably effective, if there exist no fractures or conduits in the sediment layers.


The spatial distribution of chalcophile elements in terrestrial and marine areas of Japan

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The Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology, has conducted research on the spatial distribution of 51 elements (Geochemical Maps) both in terrestrial and marine environments [1]. Japan is surrounded by vast sea, so it is important to know the spatial distribution patterns of elemental concentrations comprehensively in land and sea. This project is intended: 1) to elucidate background of elemental abundance in terrestrial and marine areas; 2) to find mass transport from land to sea or in marine environment; and 3) to estimate diffusion processes of pollutants.

Chalcophile elements such as Cu, Zn, As, Cd, Sb, Hg, and Pb are highly enriched in stream sediments associated with metalliferous deposits and anthropogenic activity. However, coastal seas sediments that were supplied by rivers flowing through metalliferous province are not significantly enriched in these elements. We assumed that the sulfide ores are oxidized, consequently releasing heavy elements in river water during transportation. However, Zn and Pb are exception. The high concentration areas of these elements are found both in terrestrial area associated with metalliferous deposits and the adjacent coastal sea area. It is possible that aqueous Zn and Pb released through oxidation process of sulfide are derived to coastal seas and sorbed on the sediment surface.

The influence of anthropogenic activity on geochemical maps is different from the case of metalliferous deposit. The concentrations of chalcophile elements are elevated in both the metropolitan area and adjacent inner bay. Chalcophile elements are enriched in the inner bay but poor in the outer bay. The spatial distributions suggest that the contaminated materials remain in the bay without extending to the outer sea. It is probable that the estuarine circulation prevents fine particles associated with chalcophile elements from reaching the outer sea because it flows from the outer sea to the bays.


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Modeling fluid migration in deep crust with modeled permeability based on wettability and energy consideration

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Under the high-temperature and high-pressure system in deep crustal setting, it is considered that fluid flows through degradative polycrystalline solid [1]. Here, the solid–liquid dihedral angle which express the wettability of the system is considered to be an important factor in determining internal pore structure, and hence, permeability [2, 3]. The pore structure is formed so as to satisfy texturally and energetically stable conditions under certain dihedral angle and fluid fraction [2, 3].

We constructed a permeability model to formulate a relationship among dihedral angle, permeability and fluid fraction by taking into consideration the textural and energetic conditions. The model is based on the assumption that there exists a fluid fraction to minimize grain boundary interfacial energy under certain dihedral angle [3]. We calculated the fluid fraction and the permeability under the “minimum” interfacial energy condition as a function of dihedral angle. The generalized permeability was described as functions of the permeability and the fluid fraction under the “minimum” interfacial energy condition.

We numerically calculated fluid migration processes by applying the modeled permeability to the governing equations formulating both solid deformation and fluid flow through polycrystalline solid. We found that fluid fraction increased with decreasing permeability in the case that the change of dihedral angle was inversely proportional to depth. By setting the solid bulk/shear viscosity to be $10^{20}$ Pa*s, fluid fraction showed repeated fluctuation. Consequently, intervals with relatively high fluid fraction were formed. Moreover, flow regime drastically changed depending on the solid bulk/shear viscosity. Our result emphasizes the importance of wettability and spatial heterogeneity of deep crust on the fluid flow processes.


A new mechanism for transport of water into CMB

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Water circulation in global Earth is one of the most important issues in geodynamics, because water can affect the physical properties including rheological property of the Earth’s materials [1]. Several hydrous minerals in subducting slabs work as water carriers or reservoirs under the conditions of the upper mantle and transition zone [2]. However, it has been debated whether water can be transported into the lower mantle and core [2]. Dehydrated water in subducting oceanic crusts by decomposition of lawsonite may be trapped as a pore fluid because of a high wetting angle between garnet and water, thus resulting in coexistence of water and aluminous MgSiO 3 perovskite, which is the major mineral in the subducting oceanic crust [3]. Here we report a new mechanism for water transport into the lower mantle and core, i.e., a reaction between aluminous perovskite and water to form alumina-depleted perovskite and δ-AlOOH [4] along the slab and mantle geotherms under the lower mantle conditions. δ-AlOOH coexists with the aluminous MgSiO 3 perovskite and post-perovskite phases in the MgSiO 3–Al 2 O 3–H 2 O system along the slab and mantle geotherms in the lower mantle. Chemical analysis of these phases revealed that the perovskite and post-perovskite phases were depleted in Al 2 O 3. Our results demonstrate the coexistence of alumina-depleted MgSiO 3 perovskite or post-perovskite phase and Mg, Si-bearing δ-AlOOH phase in wet slabs subducting in the lower mantle. Thus, Mg, Si-bearing δ-AlOOH phase thus formed transports hydrogen into the core-mantle boundary (CMB) region.

Micro-scale sensor array-enabled hot spring mapping

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Micro-scale temperature and electrical conductivity sensor arrays were fabricated. The linear temperature array consisted of 15 temperature sensors with separations of 1 cm. The linear conductivity array consisted of 5 conductivity sensors with separations of 1 cm. Both arrays were deployed in hot springs at Yellowstone National Park, USA. At one site, two geochemically different hot spring outflow channels converged. One channel was acidic (pH ~3.3, temperature ~36 °C, conductivity ~900 µS/cm). The second channel was alkaline (pH ~7.8, temperature ~60 °C, conductivity ~4200 µS/cm). Where the two streams mixed, visually distinct bands of photosynthetic pigments were observed that were not seen elsewhere in either stream.

Figure 1: Photograph showing the confluence of two hot spring outflow channels. Where the alkaline channel (top – white arrow) and the acidic channel (bottom – black arrow) mix, bands of color are observed. The location between colors is assisted with dashed lines.

More than 700 temperature and 90 conductivity measurements were taken within the mixing zone using the arrays. Extremely high spatial resolution mapping of temperature and conductivity in the mixing zone was performed. The temperature color map traces out distinct regions that match the shape and width of many of the photosynthetic pigment bands. Furthermore, the temperature data were used to predict the conductivity at a higher sampling density than was measured, providing a new technique for mapping conservative constituents at high spatial resolution in mixing zones.

Development of ETV-MC-ICPMS technique for W isotope analysis

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Hi-W chronometer is based on the negative beta-decay of r-process nuclide 182Hf to 182W with a half-life of 8.9 ± 0.1 Myr [1]. Hafnium is strongly lithophile elements, whereas W is moderately siderophile elements, and therefore, it has been well recognized that the Hi-W age provided critical information about the timing of metal-silicate differentiation (core formation) processes at the early stage of the planetary formation. Moreover, both the Hf and W is strongly refractory elements, the Hf-W age can reflect the timing of condensation or segregation of the metallic nuggets from chondritic reservoir at the early sequence of the solar system.

In this study, we have developed a new sample introduction system using an electrothermal vaporization (ETV)-MC-ICPMS technique in order to measure the isotope ratio from ng-amount of W. Compared to the conventional nebulization sample introduction technique, the ETV technique has significantly higher sample introduction efficiency. ETV-ICP technique has been accepted as a one of the most powerful tool to measure the small sample sizes[2]. With the conventional ETV system, despite the better sample introduction efficiency could be achieved, signal stability for the refractory elements, including W, was deteriorated. To obtain stable signal intensity profiles for W isotopes, He, instead of Ar, was used as carrier gas.

In our experiments, W sample in 0.5 - 1.0 µL of 2wt% HNO3 solution was loaded onto a Re filament. The filament was set into the small glass chamber (~25 mL), and then, temperature of the Re filament is controlled by the incident current (0 – 4 A) under the He gas. W signal was observed at ~1100°C. Compared to Ar gas environment, W signal stability was dramatically improved under the He gas condition. W standard solution (JMC22841) was measured several times, and the obtained 182W/184W ratios were 0.864691 ± 0.000024 from 75 ng W (n = 9) and 0.864693 ± 0.000044 from 25 ng W (n = 9) (corrected using exponential law using 186W/183W = 1.9859 [3]). In this presentation, 182W/184W ratios obtained from meteorite samples will be discussed.

Laboratory experiments on the effect of microbial activities on iodine speciation in seawater

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In seawater, iodine concentration is relatively constant (0.3 – 0.5 micro M). However, chemical forms of iodine are known to be variable and there are species of iodide (I-), iodate (IO3-) and organic iodine. Due to the oxic condition in seawater, iodate is thermodynamically stable and it is dominant. In surface seawater, iodide which is a reduced form, also exists, due to presence of microorganisms, e.g. nitrate-reducing bacteria which reduce iodate to iodide (Tsunogai and Sasa, 1969; Amachi et al., 2007). In our previous study on the speciation of iodine in pore water of marine sediments, we found the dominant species was iodide. This was explained by the anoxic condition created by the effect of microorganisms in the sediments.

In this study, we used seawater samples collected from site on Pacific Coast such as Numadu (Suruga Bay) and Odaiba (Tokyo Bay). The samples were introduced into 50 ml glass vials after following treatments; autoclaving, filtering or addition of antibiotic substances together with unfiltered fresh samples. They were incubated under light and dark conditions at 25 ºC in a laboratory. The chemical forms of iodine were determined over time using HPLC-ICP-MS.

Analytical results showed that the concentration of iodide increased and that of iodate deceased with time under light condition. This result agrees with increased iodide proportion reported in the euphoric zone. However, under dark condition, no obvious changes of iodine chemical forms were observed.

In seawater samples that were either sterilized by autoclaving or filtering, chemical forms of iodine did not change as much. These findings indicate the role of microorganisms on the transformation of iodine species.

Calcite and Chalk: Differences in Vapour Adsorption Behaviour

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Calcite is a common mineral, widely used in industry and important in environmental processes. It is the main component of chalk and limestone, which serve as natural reservoirs for water and oil. Understanding adsorption energetics and wetting properties of calcite surfaces is important for developing remediation strategies for aquifers, for improving oil recovery, for minimising risk in CO2 storage and for optimising industrial processes. We have compared the adsorption properties of synthetic calcite with those of chalk samples, composed of biogenic calcite.

We measured the heat of adsorption for water and several alcohols, from the gas phase, and determined the surface energy in order to learn more about the surface properties of these samples. XPS (X-ray photoelectron spectroscopy) was used to monitor changes in chalk surface composition when the organic content was decreased by extraction with CH2Cl2/CH3OH. The affinity for vapour of polar longer chain organic compounds (e.g. alcohols) was higher for synthetic calcite than for chalk, giving enthalpies of adsorption typical for chemisorption (>100 kJ/mole). DFT/MD (density functional theory and molecular dynamics) simulations showed that the alcohols formed structured monolayers on calcite and that dispersive lateral interactions between the CH2 tails of the adsorbed molecules contributed as much as 60% of the overall adsorption energy. Such behaviour was not observed for the chalk samples. Alcohol vapours adsorbed to chalk with lower binding energy (<80 kJ/mole), showing a distribution of adsorption energies typical for heterogeneous surfaces. After partially removing organic contamination by extraction, water and ethanol adsorption experiments showed that surface energy, mainly the dispersive component, increased. This increase might be a response to the low polarity of surface sites generated during extraction and could be connected to the presence of nanoscale clay lamellae, already seen using AFM (atomic force microscopy) chemical force mapping [1]. However, the response could also result from increased lateral interactions between the CH2 tails of alcohols adsorbed on the calcite surface of the chalk.


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Theory on thermodynamic constraints on biogeochemical diversity

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Understanding geographic patterns of biological and geological diversity is central to ecology, evolution, biogeography, and many areas of geology. The number of energy-yielding reactions—geochemical catabolic richness—imposes fundamental constraints on the number of energy-yielding reactions harnessed by a living system—the biogeochemical catabolic richness—which in turn can influence organism and ecosystem function and taxonomic diversity. Theory on geochemical and biogeochemical catabolic richness is lacking, despite its relevance to understanding evolutionary and macroecological patterns of functional and metabolic diversity. A system’s potential biogeochemical catabolic richness is the number of chemical reactions having energy-yields above some $A_{min}$ required to make the reaction useful as an energy source. We develop general mathematical theory based in thermodynamics and theoretical geochemistry showing how potential biogeochemical catabolic richness of a reaction system involving a given chemical species depends on temperature, pressure, concentration, $A_{min}$, and the frequency distribution of the species’ stoichiometric coefficients for the reactions. We then apply the theory to reactions involving H+ to provide mathematical predictions of how the community’s potential biogeochemical catabolic richness is a function of temperature, pH, and $A_{min}$. We find that the theoretical predictions closely matched empirical richness patterns of hot springs at Yellowstone National Park. The developed theory elucidates the degree to which various physicochemical variables can influence biogeochemical richness, and may have implications for patterns of functional, taxonomic and phylogenetic diversity in microbial communities.

$H_2$, $CH_4$ and $NH_4$ formation through low temperature water-rock reactions in ultramafic rock

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$H_2$, $CH_4$, and $NH_4$ are electron donors potentially important for chemolithothrophic microorganisms in subsurface endolithic communities. High-temperature formation of $H_2$ and $CH_4$ in ultramafic systems is well studied. Knowledge of low-temperature processes, and the effect of ferrous secondary minerals are however limited. Here we explore the formation of these species during experimental low temperature (25°C) alteration unaltered, medium altered and highly altered dunite from continental sites.

$H_2$, $CH_4$, $NH_4$ and $NO_3$ were detected in the fluids in all three setups. We suggest that $H_2$ results from reduction of water due to oxidation of Fe(II) released from olivine in unaltered dunite, from brucite and olivine in medium altered dunite, and from brucite and serpentinite in highly altered dunite. $CH_4$ may result from abiotic methanogenesis or dissolution of $CH_4$-containing fluid inclusions. The $N$-species were most likely absorbed to serpentinite in the altered dunite, while the source for unaltered dunite is probably explosives used during mining.

The results indicate that water-rock reactions in medium and highly altered ultramafic rocks can provide reduced species potentially supporting microbial communities in low-temperature subsurface environments in ophiolites and near seafloor parts of ultramafic oceanic lithosphere.
Ore Mineralization Processes in the Greater Caucasus Kakheti Segment, Georgia

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The Greater Caucasus represents a Phanerozoic collisional orogen which is formed along the Euro-Asian continent South margin and is expended over 1200 km between the Black and Caspian Seas. The Kakheti segment is located on the eastern part of the Greater Caucasus southern slope and is mainly formed of folded Lower Jurassic clay-shales and basic volcanic-sedimentary formations, which according to geophysical data, are located on oceanic or transitional crust (Morariu, Nouval, 2009). The complex of these rocks is intersected by Middle-Upper Jurassic gabbroic, dioritic, quartz-dioritic and felsitic intrusions which caused intensive hydrothermal silicification, sericitization and ore mineralization of the fractioned host rocks (Okrostsvaridze et al., 2012).

The above mentioned ore mineralization was studied by supported of Georgian National Science Foundation grant (#GNSF/ST09-1071-5-150). Metals chemical analyses more than 300 ore samples were carried out in the laboratory of ACMELABS (Canada, Vancouver), using ICP-MS, by 3B, 14B, F5 and 1F15 methods.

Our research showed that ore mineralization processes genetically are related to postmagmatic events of Middle-Upper Jurassic intrusive magmatism in the Caucasus Kakheti segment. Two mineralization zones - the Northern and the Southern are distinguished here. The Northern one is mainly distinguished by pyrite-polymetallic mineralization, where content of Pb and Zn sometimes is >10000 g/t, Co - varies between 40-295 g/t, and Ag – 5-95 g/t intervals. Au doesn’t have an industrial concentration (0.01-0.05 g/t) in this zone. The Southern mineralized zone is represented by copper-pyrrhotitic ores, where Cu concentration sometimes is >10000 g/t, and Au reaches industrial concentrations (0.1-3.1 g/t). At the last stage of ore mineralization, at some areas of the South mineralized zone Th and Bi concentrations are detected, which genetically should be related to carbonate hydrotherms. In these rocks Th content varies from 40 to 120 g/t, and Bi – from 200 to 800 g/t, but near the Gelia ore zone concentration of Th reaches 3842 g/t, and Bi - 4806 g/t (Okrostsvaridze et al., 2011).

Sr stable isotopic anomalies in primitive meteorites and chondrules

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Chondrules are one of the main constituents of chondrites (CC: 15-60 vol.%, OC: 60-80 vol.%, EC: 60-80 vol.%). The identification of chondrule formation mechanism is an important clue to understand how Solar System precursor solids formed, were transported, and mixed in the nebula. Interpretations of chondrules’ origins are still controversial, however, particularly because chondrule bulk compositions have a large variation in their chemical composition. In this study, we tackle this issue by analyzing highly precise Sr isotope compositions in chondrules with a variety of chemical compositions that were separated from multiple chondrites.

Chondrules were separated by a freeze-thaw method or sampled from sliced specimens by using a micro milling system (Geomill 326, Izumo) [1]. We followed the sample digestion procedure of [2]. Sr isotopic measurements were carried out by TIMS (Triton plus at Tokyo Tech). The 

Sr stable isotopic anomalies in primitive meteorites and chondrules

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Delineating biotic and abiotic carbonaceous material in the Apex chert

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The Apex chert in Western Australia has been the center of many debates about whether these rocks contain unambiguous evidence of the early biosphere. Originally, these rocks were described to contain cyanobacterial microfossils [1] although later studies have described these features as having a morphology [2] and mineralogy [3] inconsistent with life. Additionally, these rocks contain carbonaceous material (CM) of unknown origin. This CM as been described by some as being of abiotic catalytic origin [2], and by others as biogenic [4]. Although Raman spectroscopy is not sufficient in and of itself to determine the source of CM, including whether it is biogenic [5], we recently used Raman spectroscopy in a paragenetic framework to demonstrate that the CM is from at least two separate populations [6]. Here we show using high-resolution transmission electron microscopy (HRTEM) that the CM found in the Apex chert exhibits at least four different microtextures. As different types of CM have different carbon crystallinities, the sources of these microtextures can be determined, revealing CM produced by processes such as abiotic catalytic synthesis, meteoritic input, and biological synthesis.

We selected ten skeletal chondrules from the CBb chondrite Hammahal Am Harma 237 and determined their Mg isotope compositions and $^{27}$Al/$^{24}$Mg values using methods described in [4]. The chondrules show variability in the mass-dependent $\mu^{26}\text{Mg}$ component from -86±15 ppm to 292±7.1 ppm relative to Earth’s mantle) that is correlated to their $^{27}$Al/$^{24}$Mg ratios in a manner consistent with a condensation origin. Using a kinetic fractionation law ($\beta=0.511$) to determine the mass-independent $\mu^{26}\text{Mg}$* values results in a negative correlation in $\mu^{26}\text{Mg}$* and $^{27}$Al/$^{24}$Mg space, establishing that the $\mu^{26}\text{Mg}$ variability was not imparted by kinetic processes. Instead, using the experimentally determined fractionation factor of $\beta=0.514$ [5] returns a single $\mu^{26}\text{Mg}$* population with an uncertainty that is comparable with the external reproducibility of our method (∼2.5 ppm). These data indicate that CBb chondrules formed by condensation from an isotopically homogeneous reservoir 4.7 Myr after formation of canonical CAIs. The Mg-isotope composition of CBb chondrules are thus supportive of the giant impact scenario for the formation of CB chondrites.

Mg-isotopic evidence for CBb chondrule formation by condensation from an impact plume

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Chondrules are millimeter-sized spherules formed as molten droplets and are a major constituent of chondrite meteorites. Using U-corrected Pb-Pb dating, it has been shown that chondrule formation started contemporaneously with calcium-aluminium-rich inclusions (CAIs) and lasted several Myr [1]. Of interest are chondrules from the CB group, which in contrast to typical chondrules have exclusively non-porphyritic textures and magnesium-rich compositions. Their formation is believed to have occurred ≥5 Myr after CAIs, that is, much later than most chondrules. Based on these observation, it has been suggested that CB chondrules formed from a plume produced by an impact between planetary embryos after dust in the protoplanetary disk had largely dissipated [2]. However, late formation of these objects in a disk environment cannot be excluded [3]. Here, we use high-resolution Al-Mg isotope measurements to explore the formation mechanism(s) of CBb chondrules.

We selected ten skeletal chondrules from the CBb chondrite Hammahal Am Harma 237 and determined their Mg isotope compositions and $^{27}$Al/$^{24}$Mg values using methods described in [4]. The chondrules show variability in the mass-dependent $\mu^{26}\text{Mg}$ component (from -86±15 ppm to 292±7.1 ppm relative to Earth’s mantle) that is correlated to their $^{27}$Al/$^{24}$Mg ratios in a manner consistent with a condensation origin. Using a kinetic fractionation law ($\beta=0.511$) to determine the mass-independent $\mu^{26}\text{Mg}$* values results in a negative correlation in $\mu^{26}\text{Mg}$* and $^{27}$Al/$^{24}$Mg space, establishing that the $\mu^{26}\text{Mg}$ variability was not imparted by kinetic processes. Instead, using the experimentally determined fractionation factor of $\beta=0.514$ [5] returns a single $\mu^{26}\text{Mg}$* population with an uncertainty that is comparable with the external reproducibility of our method (∼2.5 ppm). These data indicate that CBb chondrules formed by condensation from an isotopically homogeneous reservoir 4.7 Myr after formation of canonical CAIs. The Mg-isotope composition of CBb chondrules are thus supportive of the giant impact scenario for the formation of CB chondrites.


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Effects of pH and ionic strength on the surface charge density of self-assembled monolayers (SAM)

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The properties of a surface depend very much on its surface charge density and polarity. Charged or highly polar surfaces are usually water wet and interact strongly with polar molecules. In some cases, such surface-organic affinities enhance organic compound adsorption. Surface charge density is therefore also important in making our society more sustainable through, for example, designing new material properties, filtering drinking water, ensuring safe CO2 storage and enhancing oil recovery. We used ionizable COOH-terminated self assembled monolayers (SAM) to investigate the effect of solvent pH and ionic strength on surface charge density. We set up three different models for the effective charge-charge interaction between neighboring COO- groups and calculated the fraction of deprotonated SAMs for various ionic strengths (figure).

Figure: Titration curves predicted using the three models for three values of ionic strength.

The effective pKₐ value of the SAM increases substantially from the monomer value at low salinity because of the increased charge-charge interaction between neighbors. As ionic strength decreases, the titration curves become flatter and deviate significantly from the standard Henderson-Hasselbalch expression. With these simulations, we obtain contour plots of the surface charge density at any pH and ionic strength. The simulations are nicely consistent with data from atomic force microscopy (AFM) chemical mapping.

Biogeochemistry of Acidic lakes in the Iberian Pyritic Belt

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The Iberian Pyritic Belt is one of the largest pyrite deposits on Earth. The exposure and subsequent oxidation of sulfide containing ores, resulting from mining activities, has lead to the formation of acid mine drainage (AMD) in this region. Acidic, metal contaminated lakes, which often form as result of the inundation of mine pits are a substantial hazard in this region. For this reason the hydrochemistry of these systems has been the subject of several studies. However, there is very little known about the sediments in these lakes and the role of benthic-pelagic coupling for these systems. We conducted an interdisciplinary study that combined geochemical, stable isotope (H, O, C, S), and microbiological tools to develop a biogeochemical model for three pit lakes: Concepción, Nuestra Señora del Carmen, and Tharsis Filón Centro.

Consistent with the oxidation of sulfide minerals, mixolimnion pH of these lakes ranged between 2 and 3, with enhanced concentrations of dissolved elements, such as SO4²-, As, Fe, Al, Mn, and Zn. ORP ranged from +600 to +400 mV and Fe(III) dominated iron speciation within these zones. In general, Fe(II), CO₂, CH₄ and pH increased in the monimolimnion of all lakes. Additionally, Eh decreased in these zones. In the sediments, pH ranged from 4 to 6 and ORP from -200 to +100 mV. Moderate sulfate reduction rates of up to 60 nmoles SO₄²⁻·cm⁻³·d⁻¹ were measured in the sediments. CO₂ and CH₄ concentrations were enhanced compared to the water column. 16S rRNA gene analysis revealed the presence of sulfate reducing bacteria as well as a broad spectrum of other bacteria, and archaea commonly associated with acidic sedimentary environments. Our results indicate that the sediments act as concentrators for organic material, resulting in microbial activity that enables the increase in pH of the sediments and bottoms waters of the lakes.
Effect of hydroxycarbonate green-rust particle size on ferrous denitrification

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Green-rusts are mixed Fe(II,III) layered double hydroxides commonly found in anoxic zones of natural environments such as sediments and hydromorphic soils, in which they control the concentration of dissolved iron in the soil solutions. In such anoxic environments, green-rust minerals play an important role in the biogeochemical redox cycling of Fe, and can affect the speciation and mobility of many organic and inorganic contaminants. Therefore, an improved understanding of the processes and/or parameters controlling the formation and growth, the particle sizes and reactivity of green-rust in natural and engineered systems may help to better managing contaminant fate. Indeed, previous laboratory studies have reported that synthetic green-rusts are capable of reducing for instance nitrate [1] and nitrite [2], selenate [3], chromate [4], Ag(I), Au(III), Hg(II) [5] and halogenated hydrocarbons [6].

In the present study, we have prepared synthetic Fe(II,III) hydroxycarbonate green-rusts [GR(CO3)] under various conditions, using various chemical procedures. Among the abiotic GR(CO3) obtained from these synthesis pathways, the most stable were aged, leading to significant particle growth. The reactivity of nano-sized and micro-sized GR(CO3) was studied in the presence of either nitrite or nitrate. X-ray diffraction and scanning electron microscopy were used to characterize solid phases of time-series samples obtained after interaction with nitrite or nitrate and show major influence of the particle size on the mass balance and the kinetics of the redox reactions investigated.


Quantitative color mapping of a brown altered granite by means of dark field reflection visible micro-spectroscopy

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Reddish brown zones often extend from fractures toward interiors of granites (Fig.1a). Such colored zones are considered to be due to the presence of iron (hydr)oxides formed by weathering and/or hydrothermal alteration. However, their chemical forms and distributions have not been well characterized by conventional analytical methods.

In this study, microscopic visible dark field reflectance spectroscopy equipped with a color mapping system has been developed and applied to a brown-colored Rokko granite sample (Fig.1b). Sample reflectance spectra show similar features to goethite, lepidocrocite and ferrihydrite. Raman micro-spectroscopy on the granite sample surface confirm the presence of these minerals. L*a*b* color values (second CIE 1976 color space) were determined from the sample reflection spectra.

Grey, yellow and brown zones of the granite show different L* a* and b* values. In the a*-b* diagram (Fig.1c), a* and b* values in the grey and brown zones are between the goethite and ferrihydrite trends, but their values in the brown zone are larger than those in the grey zone. The yellow zone shows data points close to the goethite trend. Iron (hydr)oxides rich areas can be visualized by means of large a* and b* values in the L*, a* and b* maps. The visible dark field reflectance spectroscopy with the color mapping system can be an useful method for studying distribution of colored-minerals such as iron (hydr)oxides.
Phase transformation in Fe$_2$SiO$_4$ at high pressure and high temperature

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Olivine, (Mg,Fe)$_2$SiO$_4$, is the most abundant mineral in the upper mantle. The iron content in olivine varies with depth because of chemical interactions with other mantle phases and determining the phase diagram of the polymorphs of the Fe$_2$SiO$_4$ end-member is important for precise modeling of the Mg$_2$SiO$_4$-Fe$_2$SiO$_4$ system. With pressure and temperature increase, Fe$_2$SiO$_4$ fayalite transforms into a spinel phase. The transition pressure from olivine to spinel phase has been confirmed to be around 5 GPa at high temperatures by previous experimental studies. However, the values of the $dP/dT$ slopes scatter from 2.5 to 4.5 MPa/K. This phase boundary has been used as a pressure calibration point at high temperatures in high-pressure experiment. Therefore, the precise phase boundary of Fe$_2$SiO$_4$ needs to be determined.

The starting material was Fe$_2$SiO$_4$ fayalite, synthesized from a starting mixture composed of finely powdered Fe$_2$O$_3$ and SiO$_2$. High-pressure X-ray diffraction experiments were performed using a multi-anvil high-pressure apparatus, and was combined with a synchrotron radiation source located at the KEK and SPring-8 facilities in Japan. In our experiments, pressure was applied to the sample by generating a press load. The sample was then quickly heated until it reached the desired temperature for a given press load. After reaching the required temperature, we performed in situ measurements using the synchrotron X-rays and the heating temperature was maintained for 1-3 h. At the end of the experimental runs, the sample was quenched by cutting off the electrical power. This heating procedure was the same as that used in typical quench experiments.

We report on the disputed issue of the $dP/dT$ slope of the olivine-spinel transition in Fe$_2$SiO$_4$, and establish the phase boundary with improved accuracy using our pressure and temperature data. We performed approximately 25 experimental runs to investigate the phase boundary between the olivine and spinel structures. The gradient of $dP/dT$ of the phase boundary was positive.

P (GPa) = 0.5(3) + 0.0034(3) x T (K).

The boundary determined in this study is in general agreement with those reported in previous quench or in situ high-pressure experiments. However, the $dP/dT$ slope was more positive than that in the previous in situ experiment.

Clumped Methane Isotopologue ($^{13}$CH$_3$D) Thermometry of Geological Methane by Tunable Mid-Infrared Laser Spectroscopy

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We have developed a tunable laser mid-infrared spectroscopy instrument to measure four isotopologues of methane including clumped isotopologue, $^{13}$CH$_3$D. Precise measurements of $^{13}$CH$_3$D abundance will add another critical dimension to resolve biogenic and abiogenic sources of methane in the marine and continental deep subsurface, and the atmosphere.

The new spectrometer houses two quantum cascade lasers that are tuned to a series of well resolved fundamental absorption lines in the 8 µm wavelength region. One laser measures absorption lines for $^{12}$CH$_3$D, $^{13}$CH$_3$D, and the other $^{12}$CH$_4$ and $^{13}$CH$_4$. Precisions (1σ) are 0.1% for the ratio $^{13}$CH$_4$/^{12}$CH$_4$ and $^{12}$CH$_3$D/$^{12}$CH$_4$, and 0.3 ‰ for the ratio $^{13}$CH$_3$D/^12$CH$_4$, evaluated by comparing two methane cylinder samples. Accuracy of the technique is assured by comparing δ$^13$C and δD values measured by a conventional isotope-ratio mass spectrometer.

The abundance of $^{13}$CH$_3$D is expected to reflect the temperature at which methane is thermally equilibrated, according to the isotope exchange reaction:

$^{12}$CH$_4$ + $^{13}$CH$_3$D $\leftrightarrow$ $^{13}$CH$_4$ + $^{12}$CH$_3$D

The equilibrium constant for this reaction approaches unity at very high temperatures (>1,000K). At low temperature, the above equilibrium constant deviates from unity, reaching values of 1.0066, 1.0050, 1.0011 at 0, 100 and 400 °C, respectively. Therefore, the precision of 0.3 ‰ would permit a temperature estimate of ±10°C for methane formed or scrambled at 25°C. The measured ‘clumped isotope temperature’, however, is expected to be biased when mixing of two or more sources of methane occur due to some non-linearity in the ratio $^{13}$CH$_3$D/$^{12}$CH$_4$ upon mixing. We will discuss some preliminary data and the potential of this new approach to delineate deep subsurface methane sources and their role in the deep carbon cycle.
Meteorite impact, volcanism, and radiolarian faunal turnover recorded in the Upper Triassic of Japan

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The Late Triassic was characterized by several marine and terrestrial biotic turnover events prior to the end-Triassic mass extinction. The causes of the end-Triassic mass extinction and these Norian to Rhaetian biotic turnover events are still the subject of debate. Catastrophic processes such as widespread eruption of the Central Atlantic Magmatic Province (CAMP) flood basalts and extraterrestrial impacts have been proposed to account for the biotic turnover events [1, 2]. Here, we report a marine osmium (Os) isotope record reconstructed from an upper Triassic bedded chert succession in Japan, which accumulated on the paleo-Pacific deep seafloor. We also analyzed the extinction patterns of Late Triassic radiolarian species from the bedded chert succession with the marine Os isotope record.

The Os isotope data show an abrupt and marked negative excursion from an initial Os isotope ratio of ~0.477 to unradiogenic values of ~0.127 in a claystone layer within a middle Norian bedded chert (~215 Ma), indicating the input of meteorite-derived Os into seawater [3]. A gradual decrease in 187Os/188Os ratio during the Rhaetian (201–210 Ma) is considered to have been closely linked to the CAMP volcanic event [4]. An analysis of radiolarians provides no indication of a mass extinction event across the claystone layer and during the CAMP volcanic phase. However, a significant faunal turnover occurred at ~1 Myr after the impact event. Biostratigraphic analysis shows that 20 radiolarian species became extinct at this level in the chert. It is possible that the impact triggered the extinction of these 20 species, though the direct cause of their extinction remains uncertain.


The influence of the stoichiometry of arsenopyrite on the impurity density

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The chemical composition of arsenopyrite FeAsS may differ in detail from one deposit to another, from one deposition stage to another, and even from the outer parts of a single grain towards its interior. Based on a comprehensive analysis of the crystal structure, chemical and phase composition of the analytical expressions for the calculation of the impurity density in the arsenopyrite received. The algorithm for calculating the impurity density structures such as NiAs proposed Onufrienok (Onufrienek et al., 2012). To calculate the density impurities into arsenopyrite was amended. The impurity density for the impurity atoms cobalt Co, copper Cu, nickel Ni and gold Au is calculated separately. Specimens for investigated from the deposit Panibma Krasnoyarsk region. Studies have been conducted on ~65 samples from different mines. One such series is presented in Table 1.

Table 1: Results of the microprobe analysis (α) and the results calculations of the density impurity (β) into the arsenopyrite.

<table>
<thead>
<tr>
<th>(S/Fe) + (As/Fe)</th>
<th>cobalt Co</th>
<th>nickel Ni</th>
<th>copper Cu</th>
<th>gold Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>α %</td>
<td>β, 10^3</td>
<td>α %</td>
<td>β, 10^3</td>
<td>α %</td>
</tr>
<tr>
<td>1.9627 0.16</td>
<td>0.547</td>
<td>0.021</td>
<td>0.069</td>
<td>-</td>
</tr>
<tr>
<td>1.9467 0.18</td>
<td>0.613</td>
<td>-</td>
<td>0.007 0.216</td>
<td>0.061 0.792</td>
</tr>
<tr>
<td>1.9328 0.30</td>
<td>0.996</td>
<td>0.076</td>
<td>0.251</td>
<td>-</td>
</tr>
<tr>
<td>1.9690 0.18</td>
<td>0.621</td>
<td>0.006</td>
<td>0.019</td>
<td>-</td>
</tr>
<tr>
<td>1.9552 0.17</td>
<td>0.578</td>
<td>0.012</td>
<td>0.039</td>
<td>0.014 0.433</td>
</tr>
<tr>
<td>1.9866 0.82</td>
<td>2.746</td>
<td>0.016</td>
<td>0.053</td>
<td>0.058 1.795</td>
</tr>
<tr>
<td>1.9646 0.52</td>
<td>1.716</td>
<td>-</td>
<td>0.019</td>
<td>0.588 0.040</td>
</tr>
<tr>
<td>2.0020 0.51</td>
<td>1.694</td>
<td>0.436</td>
<td>1.444</td>
<td>0.017 0.527</td>
</tr>
<tr>
<td>2.0106 0.25</td>
<td>0.832</td>
<td>0.328</td>
<td>1.086</td>
<td>-</td>
</tr>
<tr>
<td>2.0157 0.28</td>
<td>0.954</td>
<td>0.209</td>
<td>0.692</td>
<td>-</td>
</tr>
<tr>
<td>2.0340 0.45</td>
<td>1.490</td>
<td>-</td>
<td>0.013</td>
<td>0.403 0.010</td>
</tr>
</tbody>
</table>

Because of the large scatter of the experimental points should speak not about dependencies but only a trend. As it is shown in the table, tendency to increasing of the density impurities with increasing nonstoichiometry is installed. Stoichiometric composition should be considered when the ratio (As + S)/Fe is equal to two. Decreasing this ratio impurity density tends to decrease. Statistical analysis of all samples (~65) confirmed the findings.

Marine Cements and the Late Cretaceous to Cenozoic History of Magnesium, Strontium, and Calcium in the Ocean

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Relatively unaltered ‘pristine’ marine cements from neritic environments are recognised as some of the best known proxies for recording marine chemistry through geologic time. Unfortunately, due to their metastable nature they are rarely preserved in the rock record. We have been fortunate enough to recover two examples of such cements from ancient reef environments; one from Site 877 of Leg 144 of the Ocean Drilling Program and one from a RV Melville survey in the Gulf of Papua in 2004. Both were preserved because they were tightly cemented on rapidly subsiding reef platforms and not subject to meteoric diagenesis.

The ODP sample is Maastrichtian in age and the Gulf of Papua sample is from the Early Miocene. These two time intervals represent extremes in the history of strontium incorporation into shallow water depositional environments. During the Late Cretaceous scleractinian corals (which take up large quantities of strontium into their skeletons) were relatively rare, whereas the Early Miocene represents the acme of modern style coral reef growth, with scleractinian corals abundant.

The marine cements record an Early Miocene strontium concentration that is a third of the Late Cretaceous value. Strontium concentrations are similar to or lower than comparable Holocene cements. Magnesium-calcium ratios drop to approximately 3.6 for the Early Miocene and near 2 in the Late Cretaceous. Mass balance of calcium fluxes through over the past 100 million years indicate that the alkalinity has not changed dramatically over this interval. If we hold this total relatively constant then these data confirm previously documented trends in magnesium calcium ratios and for the first time document a significant increase in strontium concentrations in the oceans of the Late Cretaceous relative to the late Cenozoic values.

Changing riverine silicon isotope delivery to the ocean over glacial-interglacial intervals? Evidence from glaciated basaltic terrains

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The marine primary production is dominated by diatoms which largely depend upon the riverine silicon delivery to the ocean. In paleoreconstruction of Si utilisation by diatoms, a constant Si isotope input from the continent to the ocean is generally assumed. In this study, glacier-fed and direct runoff rivers draining basaltic catchments in Iceland display significantly different dissolved Si isotope compositions, with lighter values ($\delta^{30}$Si = +0.17±0.18‰) associated with the high physical erosion rates in glacial rivers, and heavier values ($\delta^{30}$Si = +0.97±0.31‰) associated with lower physical erosion rates and enhanced formation of secondary minerals in direct runoff rivers. The riverine Si isotopic compositions correlate with those of Li and provide evidence of a climatic dependence that is likely to have led to glacial-interglacial differences in the isotopic composition of Si delivered to the oceans. Based on existing $\delta^{30}$Si from diatoms in a sediment record from the Southern Ocean, the interpretation of changes in Si utilisation between the Last Glacial Maximum (LGM) and the early Holocene is revisited accounting for changing Si isotope delivery to the ocean over glacial-interglacial intervals. The results are consistent with a lower Si utilisation during the LGM (53±5%) relative to the Holocene (88±5%). During the LGM, Si utilisation values are slightly higher when allowing for changing Si isotope input to the ocean (53±5%), than when a constant Si isotope input is considered (42 to 47±5%). This study suggests that changes in Si isotope delivery to the ocean should be accounted for in the precise reconstruction of ocean Si utilisation and primary productivity over glacial-interglacial timescales.
Cold-water coral biomineralization in
high resolution

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Deep-sea scleractinian skeletons are primarily precipitated along a longitudinal growth axis but also expand radially forming layers. A LA-ICP-MS track at a resolution of 15 \( \mu \text{m} \) across radial layers revealed sharp peaks in U\(^{238} \) concentrations and almost perfect antithetical behaviour of Mg\(^{25} \) and U\(^{238} \) (fig. 1). The peaks are preceded by slightly offset minima in Ba\(^{137} \) which generally follows Mg for most of the growth. Uranium peaks align with the last precipitates of visible layers before the onset of the next (often white) layer and increase of U\(^{238} \) values.

Figure 1: Ba, Mg and U concentrations (weighted at 8%) across the coral wall from outside (left) to inside (right).

The strong antithetical behaviour of U\(^{238} \) and Mg\(^{25} \) and the known negative correlation of U/Ca concentrations in corals and CO\(_3^{2-} \) in seawater [1] invite an interpretation as variations in growth rates in the corals. The short steep increases in U\(^{238} \) concentrations will be discussed as phases of low CO\(_3^{2-} \) and Mg\(^{2+} \) availability, and accordingly lower growth rates. The U peaks are preceded by minima in Ba\(^{137} \) which functions as a nutrient proxy [2]. Repeating peaks in Barium might connect variations in growth rate with regular nutrient input from surface primary production or nepheloid layers. \( \delta^{13} \)C ratios will be included in those discussions.


Oxygen and carbon cycling in
basaltic crust

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Oceanic crust is the largest potential habitat for life on Earth and may contain a significant fraction of Earth’s total microbial biomass, yet little is known about the form and function of life in this vast subseaﬂoor realm that covers nearly two-thirds of the Earth’s surface. A deep biosphere hosted in subseaﬂoor basalts has been suggested from several lines of evidence; yet, empirical analysis of metabolic reaction rates in basaltic crust is lacking. The first measure of oxygen consumption in young (~ 8 Ma) and cool (<25 °C) basaltic crust is calculated from modeling oxygen and strontium profiles in basal sediments collected during Integrated Ocean Drilling Program (IODP) Expedition 336 to ‘North Pond’, a sediment ‘pond’ on the western flank of the Mid-Atlantic Ridge (MAR). Dissolved oxygen concentrations increased towards the sediment-basement interface, indicating an upward diffusional supply from oxic fluids circulating within the crust. Furthermore, evidence of biological carbon fixation in basalt bioﬁlms comes from stable isotope incubations, with implications for carbon cycling in oceanic crust. Long-term microbiology experimentation in crustal subseaﬂoor observatories at the Juan de Fuca Ridge flank and at North Pond are poised to yield exciting new discoveries about the dynamics of microbial activity and community structure in the crustal subsurface.
Newly revealed NNW shift of granitic magmatism during Mid-Miocene period, Kyushu, Japan

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Mid-Miocene granitic plutons, related to subduction of young Shikoku Basin of the Philippine Sea (PS) plate after immediate clockwise rotation of SW Japan, are sporadically but widely distributed along the Nankai Trough in the outer zone of SW Japan (e.g., [1]). Kyushu Island is located on western part of the outer zone. This study newly determined precise U-Pb ages for felsic dikes and granitic bodies of six locations; Tanegashima, Yakushima, Minami-Osumi, Osuzuyama, Takakumayama and Okueyama, by using LA-ICPMS technique [2]. The obtained U-Pb ages ranged from 15.6 Ma to 13.7 Ma and showed negative correlation to their distances from the Nankai Trough (see below figure). Shift rate of the granitic magmatism is 4.6 cm/year with NNW direction, which is almost same to that of recent plate movement of the PS plate (4.8 km/year). Considering that the shift rate is reflected to the subduction of the PS plate, the subduction angle in Mid-Miocene is estimated as ca. 17 degree, which is almost same to that of recent PS plate on Shikoku Island. In Kyushu Island, however, the recent angle becomes max. 60 degree and Plio-Quaternary arc volcanism makes apparent volcanic front. This suggests that the PS plate during Mid-Miocene period has been shallowly subducted and subsequently slab rollback has been occurred due to slab-pushing caused by lateral flow of ashenospheric upwelling of the Ryukyu Trough [3] and/or other unknown tectonic events.


Authigenic carbonates as dynamic microbial ecosystems: expanding views of methane cycling in the deep sea

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Sulphate-dependent anaerobic oxidation of methane (AOM) is the dominant sink for methane along continental margins, oxidizing significant fraction of methane in anoxic sediments prior to its release to the hydrosphere. The alkalinity generated during this process frequently results in the precipitation of δ13C-depleted authigenic carbonates, which vary in morphology, size, and mineralogy, ranging from micritic cements and cm-sized concretions to massive ‘chemoherm’ structures, mounds, and pavements that can cover hundreds of square meters. These methane-derived structures often persist long after the flux of methane subsides, with remnant methanotrophic biomarkers recovered from paleo-seep carbonates dating back to the Paleozoic. While these authigenic carbonates have long served as important indicators of methane seepage, they are frequently discussed as passive recorders of prior seep activity, rather than as an active microbial habitat. Using a combination of molecular and geochemical analyses, rate measurements, stable isotope labelling experiments and nanoscale secondary ion mass spectrometry (nanoSIMS), we examined the potential for these systems to sustain active methanotrophic microorganisms and documented changes in the microbial community associated with areas of active methane venting and sites of low methane flux. Here we demonstrate that authigenic deep-sea carbonates 1) host abundant methanotrophic archaea and sulphate-reducing bacterial consortia, 2) are actively oxidizing methane 3) are capable of growth and incorporation of methane into biomass 4) provide a unique habitat and food source for seep-associated meio- and macrofauna. Seafloor calcite and dolomite incubations, transplant experiments and in situ collections of carbonates show differences in the dominant methanotrophic archaea (ANME-1 vs. ANME-2) and methane-oxidation rates related to levels of methane seepage and possibly mineralogy, with viable endolithic methanotrophic archaea and above background levels of methane-oxidation documented in authigenic carbonates well outside areas of visible methane seepage. Together, this data indicate that authigenic carbonates are living and actively evolving ecosystems and represent a previously underappreciated sink for methane.

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Measurement of light extinction by single aerosol particles


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Cavity ring-down spectroscopy (CRDS) is increasingly being used to determine extinction of light by ensembles of aerosol particles, either in the laboratory or in field measurements. Under controlled laboratory conditions, with size-selection of the aerosol particles prior to CRDS detection, extinction efficiencies and refractive indices can be determined. However, the precision and accuracy of such ensemble measurements are limited by a number of factors inherent in the experiments [1,2]. One significant source of uncertainty is the distribution of sizes of the aerosol particles passing through the differential mobility analyser employed as the size-selecting device.

We have therefore developed a CRDS-based method to determine the optical cross sections and extinction efficiencies of single aerosol particles of diameter ~ 1 µm or less. A Bessel beam optical trap is used to confine and manipulate the position of the single aerosol particle. Particles smaller than 1 µm can be captured indefinitely and we have demonstrated the ability to study processes that change the size or refractive index, such as the evaporation of volatile components or the uptake of water. The measured extinction induced by the particle depends on the position of the particle within the cavity [3,4], so fine positional control is required. Results will be presented for a number of aerosol particle compositions. For example, the variation in extinction efficiency of a single trapped sodium chloride droplet with relative humidity agrees very well with predictions from Mie scattering theory. The advantages of single-particle over ensemble measurements will be discussed.


Temperature reconstruction for the last 1000 years at WAIS-Divide, Antarctica, from inert gas isotopes and borehole temperature.

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West Antarctica is warming, but it is not clear yet whether it is abnormal, in the context of natural background variability. The amplitude of natural climate variability on multi-decadal timescales remains poorly quantified, but it is essential to our understanding of the significance of the warming of the last 50 years.

Here, we present a 1000-year temperature record at WAIS-Divide, in the center of West Antarctica, reconstructed from the combination of inert gas isotopes from the ice core and borehole temperature measurements. Borehole temperature provides an absolute estimate of long-term trends, while noble gases track decadal to centennial scale changes. This method provides a temperature reconstruction that is independent of the water isotope of the ice, and allows us to improve our understanding of water isotopes as a temperature proxy at this site.

We found that the "Little Ice Age" cold period of 1400-1800 was 0.52°C colder than the last century, and that 50 to 100 year variability is on the order of 0.5 to 1°C.
**Gene expression in the deep biosphere**

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Microbial community metabolism in the marine subsurface likely plays an important role in global biogeochemical cycles but deep biosphere activities are not well understood. Illumina sequencing of community messenger RNA was performed to obtain the first subseafloor metatranscriptome from anaerobic Peru Margin sediment up to 159 meters below seafloor. Metabolic reconstruction indicates anaerobic metabolism of amino acids, carbohydrates, and lipids are dominant processes, and profiles of dissimilatory sulfate reductase transcripts are consistent with sulfate concentration profiles. Moreover, cell division transcripts across all three domains of life increase where peaks in microbial abundance are observed in subseafloor sulfate-methane transition zones. These data support calculations and models of subseafloor microbial metabolism, and represent the first holistic picture of deep biosphere activities. Furthermore, an investigation of eukaryotic 18S rRNA revealed active Fungi across a range of marine subsurface provinces. Subseafloor fungal populations exhibit statistically significant correlations with total organic carbon, nitrate, sulfide, and dissolved inorganic carbon suggesting environmental selection of active Fungi in the marine subsurface.

**Raman Spectra And Microhardness Of Sphalerite Solid Solutions ZnS·FeS**

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Synthesized sphalerite solid solutions (Fe\(_x\)Zn\(_{1-x}\)S) in the range 0 <mol% FeS <50 with compositional step 5 have been studied with the use of Raman spectroscopy. The main objective of these experiments was to learn how the iron content of sphalerite affects the Raman spectra [1].

Raman intensities over the whole range of concentrations suggest a structure change in the rather narrow region of mole fractions of FeS between 0.15 and 0.25. Currently special attention was paid for compositions 0 mol% FeS 6 (15 samples, gas transport and average diameter of crystals 1 mm) where microhardness (HV) grows extremely from 1.7 to 2.1 GPa. In this composition area additional peak 310 cm\(^{-1}\) appears that might be due to cluster forming process in sphalerite lattice. The ratio of intensities of Raman lines 295 and 345 cm\(^{-1}\) can be used for the compositional analysis of sphalerite.

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Vertical transport of black carbon over East Asia during the A-FORCE aircraft campaign

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The Aerosol Radiative Forcing in East Asia (A-FORCE) aircraft campaign was conducted over East Asia in March-April 2009 [1]. We examined vertical transport mechanisms of black carbon (BC) aerosols and their transport pathways over East Asia in spring using the modified version of the CMAQ model and simulating the A-FORCE aircraft campaign. Comparisons of the model results with the A-FORCE observations show that the model reproduces relatively well the vertical distributions of mass concentration and transport efficiency of BC, including their latitudinal gradients and dependences on precipitation that air parcels had been experienced during transport. During the A-FORCE period, we find two types of pronounced upward mass fluxes of BC from the planetary boundary layer (PBL) to the free troposphere (FT) over northern-eastern and inland-southern China. The major uplifting mechanism of BC over northern-eastern China is the cyclones with modest amounts of precipitation. Cumulus convections and orographic lifting along the high-altitude mountains play an important role for the upward transport of BC to the FT over inland-southern China, in spite of the large amounts of precipitation. In addition to the outflow in the PBL over the midlatitude, the upward transports over northern-eastern and inland-southern China, followed by the westerly transports in the lower and the middle FT, respectively, make major contributions to the exports of BC from East Asia to the Pacific in spring.


Precipitation and stability behaviour of calcium sulfate: the role of salinity, temperature and reaction time

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A marked inconsistency exists between the phase diagram of calcium sulfate and its crystallization behaviour [1]. To gain a better understanding on the precipitation dynamics and stability region of each phase (gypsum, bassanite and anhydrite), a series of precipitation experiments were carried out from 40 to 120 ºC, at three salinities (0.8, 2.8 and 4.3 M NaCl) and different reaction times (from 2 min up to 10 months).

Salinity and temperature strongly influence the type and stability of the precipitate. No primary anhydrite precipitation occurs and with increasing salinity bassanite precipitation prevails and its stability is strongly enhanced (up to 10 months at 80 ºC). Phase transition occurs through dissolution of the less stable phase and subsequent recrystallization of the more stable phase. This process is controlled by the differences in surface free energy and step kinetic coefficients between the three phases [2-4].

Testing the “deep-basin high-rank gas machine” hypothesis

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During the past decade the interest in a more detailed understanding of processes during gas and oil formation has been spurred by growing importance of gas and oil from unconventional reservoirs, e.g. shale gas and shale oil as well as deep basin-centered gas. In addition to the classical view of mainly first-order reactions for the inorganic formation of hydrocarbon gases by thermal cracking of bitumen or kerogen, several researchers have put forward avenues to explain some not accounted for observations in hydrocarbon occurrences, molecular or isotopic compositions. These hypotheses always include a geologic component not considered in most kerogen/bitumen pyrolysis studies: The presence and role of water [1], the possible catalytic activity of mineral surfaces [2], the importance of metals in aqueous fluids, the metastable equilibria of hydrocarbons and more oxidized organic compounds in pore-fluids in the subsurface – and the role of minerals as part of pore-fluid redox- or pH-buffers [3]. Price [4] combined many of the aforementioned hypotheses in calling for a “deep-basin high-rank gas machine”.

A broad study to produce a consistent data set of HC formation rates and elemental transfer reactions in the gas-fluid-rock system at elevated pressures and temperatures is ongoing at the BGR. By using different experimental facilities for maturation of organic matter from small gold capsules to Dickson-type flexible gold-titanium cells in high-pressure reactors to large diameter high pressure reactors for heating/expulsion tests on core material several key questions are being addressed.

The experiments with source rock material of natural maturity series allowed the detailed comparison of effects of natural medium-temperature/high-pressure maturation in the sedimentary basin to artificial high-temperature/high-pressure maturation in the lab. Interestingly, a clear depiction of the predominance of different processes – e.g. thermal cracking, oxidation reactions to less reduced organic compounds, dehydrogenation by cyclization and aromatization - is visible in the data sets. The comparison of sets of experiments with the identical amounts of source rock material with/without the admixture of different mineral standards – e.g. carbonate, pyrite, montmorillonite – yielded clues about the role of certain mineral surfaces for catalytic oxidation/dehydrogenation/hydrogenation and fluid buffering. Using organic model compounds with isotope labels added to the source rocks clearly identified pathways of hydrocarbon gas formation – and the production of more oxidized organic compounds.


Anaerobic methane oxidation in the water column of the eutrophic sub-alpine Lake Zug (Switzerland)

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Anaerobic oxidation of methane (AOM) remains only partially understood in freshwater environments. Water column field investigations suggest that AOM could be mediated via other pathways, i.e. denitrification or metal oxide reduction, in lakes [1, 2], as opposed to its marine counterpart, where AOM proceeds via SO42− reduction [3].

The potential for AOM was assessed in the water column of the eutrophic sub-alpine Lake Zug, situated in Central Switzerland. Through geochemical profiling and flux calculations of the relevant factors, the oxic/anoxic transition zone and anoxic depths, showing favorable conditions for AOM, were identified. At these selected depths, incubation experiments were carried out with 13C-labelled methane to determine methane oxidation rates, simultaneously in-situ available electron acceptors were monitored. Fluorescence in-situ hybridization targeting Group I and II as well as anaerobic methanotrophs was carried out at the incubation depths. Furthermore, functional gene analysis for particulate (pmoA) and soluble methane monoxygenase (mnoX), both essential for aerobic methanotrophs, and methyl coenzyme M reductase (mcrA), an indicator for anaerobic methanotrophs, was completed.

Preliminary experiments show that AOM rates are one order of magnitude higher (~600 nM•d−1) than aerobic rates (~40 nM•d−1). Highest rates occur at depths, which are devoid of oxygen. First results are still inconclusive as to which electron acceptor is responsible for AOM, however, SO42− does not appear to contribute substantially. Hybridization techniques confirm the presence of Type II alpha-proteobacterial methanotrophs as well as Group I and II methanotrophs.


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Chromium Enrichment in sedimentary rocks deposited in shallow water in the 3.2 Ga Moodies Group, South Africa

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Although the temporal change in trace element concentrations in Banded Iron Formations (BIFs) can be useful in reconstructing Earth’s Precambrian surface environments and associated biological activity, BIFs from various sedimentary settings, particularly of Archean age, will be investigated to increase our understanding of these environments. In this study, we investigated geological, petrographic and geochemical characteristics of ferruginous rocks deposited in a shallow water environment in the Moodies Group, in the Barberton Greenstone Belt, South Africa. Samples were obtained from an outcrop in the Moodies Hills Block and at a cross cut in the Sheba mine.

The petrographic relationships between hematite and magnetite in the samples resemble those observed in typical oxide-type BIFs. Geochemical data show that Fe and Cr are enriched relative to Ti in the ferrous rocks. Although various detrital minerals are observed, including detrital quartz, the proportion of refractory elements and rare earth element (REE) patterns show that the sediment was predominantly derived from felsic rocks. Therefore, the results of geochemical analyses of these rocks indicate that both Fe and Cr are chemical precipitates or of an early diagenetic origin. Oxygen isotope analyses of individual chromite grains by Secondary Ion Mass Spectrometry (SIMS) reveal that they are depleted in $^{18}$O compared to previously reported values for magmatic chromite, indicating that the chromite was formed under sub-magmatic temperatures (e.g., hydrothermal). Therefore, our detailed petrographic and geochemical investigations of the chemical and clastic sedimentary rocks show that some geochemically important elements (i.e., Fe, Cr, and U) were already mobile and fixed in a shallow water environment at 3.2 Ga.

Dissolution of Amorphous Silica in the Presence of Ca$^{2+}$ and Mg$^{2+}$ at pH 6 and 9

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Silica dissolves into natural waters as monosilicic acid (Si(OH)$_4$) through a break of siloxane bonds by attack of water molecule. Factors controlling the silica dissolution reaction are important subject in geochemistry to elucidate circulation of silicon in hydrosphere. Especially, because an alkaline and alkaline earth metal ions exist abundantly in natural water, the effect of these metal ions on the dissolution of silica has been investigated and the acceleration of the dissolution of silica has been reported. However, the acceleration mechanism of dissolution of silica by cations has been uncertain even at present. In the previous studies, only the variation of silicic acid concentration was mainly examined. No researcher has been investigated quantitatively the behavior of cations during the dissolution reaction. The purpose of this study is to elucidate the effect of Ca$^{2+}$ and Mg$^{2+}$ on the dissolution of silica from both the variation of silicic acid concentration with time and behavior of Ca$^{2+}$ and Mg$^{2+}$.

From the behavior of Ca$^{2+}$ and Mg$^{2+}$ during the dissolution of silica, it was revealed that the acceleration mechanism of each metal ion was clearly different by reaction pH. At pH 9, the dissolution of silica is controlled by the interaction between Ca$^{2+}$ and Mg$^{2+}$ and silicic acid: the formation of Ca$^{2+}$-silicic acid complex and of an insoluble magnesium silicate-like structure. Although no adsorption of Ca$^{2+}$ and Mg$^{2+}$ ions occurred at pH 6, the dissolution of silica was accelerated. This may be caused by attack of water molecules to siloxane bonds hydrated to Ca$^{2+}$ and Mg$^{2+}$ ions due to fast exchange reaction with the bulk water near the surface of silica.

CSD, crystal shape and connectivity in synthetic basalt from 3D reconstruction by X-ray CT image

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In-situ observation of plagioclase crystals in synthetic basalt by using micro-tomography beam lines at SPring-8, is supported from two previous experimental studies realized on same run charge [1,2]. It is here proposed to quantify crystal agglomeration and connectivity (touching crystals/non touching crystals) during crystallization and also to improve corrections applied in 2D CSD. By using micro-tomography beam lines and softwares (©Slice and ©Blob3D), three-dimensional images of the run products at a resolution of 2.74 µm are created. Size and shape evolution during cooling are clearly outlined by variation of the shape factor. A first comparison between 2D/3D CSD shows similarity in the CSD morphology. The connectivity (Fig. 1) between plagioclase crystals increases very rapidly with a ratio of 0.2 to 0.4 in the early stages of crystallization (5% plagioclase crystals) to 1 for 20-25 % of plagioclase crystals in the late stages. Processes of crystals agglomeration do not appear of major importance compared to connected crystals that form a continuous 3D network. This early crystal network strongly influences magma rheology.

Fig. 1: Plagioclase crystallinity function of plagioclase connectivity


Marine aerosol activation to CCN and cloud formation


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Marine aerosol occurring in cloud condensation nucleus (CCN) sizes suggest that it may contribute notably to the CCN population [1, 2], but further cloud droplet number concentration (CDNC) would strongly depend on the ambient (cloud) conditions, such as available water content, supersaturation and competition between the CCN of different composition [3]. Since the global importance of marine aerosol particles to the cloud formation was postulated several decades ago [4], it has progressed from the evaluation of the nss-sulphate and sea salt effects to an acknowledgement of the significant role of organic aerosol [5]. It was demonstrated that primary marine organics, despite its hydrophobic nature, can possess the high CCN activation efficiency, resulting in the efficient cloud formation [6]. Here we show the relationship between the marine boundary layer aerosol composition, CCN activation and CDNC for different aerosol and ambient conditions. We investigate the activation of sea spray composed of the sea salt and externally mixed with nss-sulphate as well as the sea spray highly enriched in organics, stressing the importance of the latter to the formation of the cloud droplets. We also explore the suitability of existing theories to explain the different composition marine aerosol activation to CCN and resulting CDNC.

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Dating zircons from volcanic ash beds in sedimentary successions: magmatic crystallization vs. ash deposition

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Detailed calibration of the Late-Middle Triassic time-scale requires precise and accurate age determinations from volcanic ash beds within biostratigraphically well dated marine sedimentary sections. High precision CA-ID-TIMS U-Pb zircon dates on volcanic zircon have been used to quantify and calibrate different stratigraphic schemes across the Early-Middle Triassic boundary in South China. Despite an optimal control on the continuity of the stratigraphic record and on the accuracy of analytical procedures, some single ash-beds from the Monggan Wantuo section (Luolou Fm., NW Guangxi, S. China) yield ages that are too old and contradict the stratigraphic succession. How can we improve the confidence in the interpretation of zircon dates as proxies for the age of deposition of these ash beds?

We dated 15 individual ash beds within the 15m Wantuo Mongan section, applying CA-ID-TIMS techniques on a number of single grains for each sample. In 13 out of 15 ash beds zircon dates are following the stratigraphic succession within analytical uncertainty (from the late Early Triassic Luolou Formation – 248.08 ± 0.12 Ma. to the Middle Anisian Transition Beds – 246.43 ± 0.17 Ma). The zircons from two intermediate volcanic ash beds within the Transition Beds at the Early/Middle Anisian boundary yield well clustering 206Pb/238U dates at 247.10 ± 0.15 and 247.35 ± 0.11 Ma, clearly indicating that the zircons in this magma batch were crystallizing over a long period of time or remobilized from deeper levels within the same magmatic system. The problem of recurrent zircon dates in a sedimentary succession is common and can only be discovered by sufficiently dense sampling and a sufficient number of data for each ash bed.

We have to keep in mind that for the correct interpretation of dates in stratigraphic sections interlayered with fossil-bearing rocks we need: i) at least one single well preserved stratigraphic section with sufficient chronostratological (biochronology and/or chemiostratigraphy) to guarantee that the stratigraphic succession is accurately known; ii) volcanic ash beds that are undisturbed (no volcanosedimentary material, no sedimentary reworking); (iii) sufficient sample and data density to be able to distinguish between magmatic and sedimentary signals coded in the crystallization ages of zircon.

The Thrym Complex of southeastern Greenland: Evolution of Ni-Cu-sulfide mineralization in the lower crust

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The Thrym Complex of southeastern Greenland forms part of the North Atlantic Craton and is characterized by migmatitic orthogneiss, narrow bands of mafic granulite, ultramafic rocks, paragneiss, and alkaline-carbonatitic intrusive rocks. The narrow bands of mafic granulite are interpreted as tectonically emplaced gabbroic rocks exposed from the lower crust.

The two main styles of mineralization locally observed in the Thrym Complex are: (1) disseminated sulfides associated with mafic and ultramafic locally granoblastic-decussate rocks; and (2) remobilised sulfides concentrated in amphibolite-greenschist facies shear zones. This mineralization observed differs from typical orthomagmatic Ni-Cu-sulfide occurrences common in the upper crust in that there is no evidence for significant contamination by a crustal sulfur source. Furthermore, no trans-lithospheric structure for the emplacement of the mineralization is apparent.

The sulfide mineralization in the Thrym Complex may represent the root of such a system or the result of a similar magma being emplaced in the lower crust in an area lacking such a fluid-pathway. Mantle-sourced magma emplaced at pressure-temperature conditions in the lower crust would maintain or achieve sulfur-saturation more easily than magma emplaced in the upper crust [1]. As such, there may be no need for interaction with crustal material for the formation of sulfide mineralization in lower crustal settings.

Trace metal drawdown during a Cretaceous oceanic anoxic event: Implications for global redox conditions

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The global redox state of the oceans during periods of widespread organic-carbon deposition is an essential part of our understanding of Earth’s important climatic feedbacks. The Cretaceous is renowned for several global organic-carbon burial events marked by coeval positive carbon isotope excursions now widely known as oceanic anoxic events (OAEs). Here we present a high-resolution compiled data set from Demerara Rise spanning the Cenomanian-Turonian boundary event (~93.9 Ma) or OAE 2, which shows a dramatic drawdown of redox sensitive trace elements. Organic carbon contents are high throughout the entire section analyzed, and, importantly, Fe speciation implies the locality was dominantly euxinic (i.e., anoxic and sulfidic bottom waters) before, during, and after the event. Molybdenum (Mo) and vanadium (V) are effective paleoredox proxies for tracing oceanic euxinia and anoxia, respectively. The drawdown of Mo coincides with the onset of OAE 2, suggesting a global expansion of reducing and sulfidic conditions. Significantly, though, the drawdown of these two redox sensitive elements is offset by 100 kyr, with V preceding Mo. The decline in V enrichment prior to Mo implies an expansion of low oxygen but non-euxinic conditions prior to the OAE. Numerical geochemical box modeling for Mo suggests that euxinia must have covered >2% but <10% of the global seafloor to explain enrichments that were only 25% of those seen before and after the event. Mo and V drawdown may have impacted the nitrogen cycle and thus patterns of primary production, and this feedback may have contributed to the termination of the OAE.

Chemical compositions of soluble aerosols around the last termination in the NEEM (Greenland) ice core

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The polar ice cores provide us with reconstruction of past atmospheric aerosols. Soluble aerosols in both Arctic and Antarctic ice cores are well discussed by using the proxy of ion concentration/flux, however, there are few studies about chemical compositions of soluble aerosols in ice cores. Using sublimation method [1], here we show differences in the compositions of sulfate and chloride aerosols around the last termination in the NEEM ice core. A total of 43 samples were distributed from NEEM ice core section from 1280 to 1580 m. Soluble aerosols were extracted from the samples by sublimation system [1]. Constituent elements and diameter of each non-volatile particle were measured by SEM-EDS. By using a method in ref. [2], we assumed chemical compositions of sulfate and chloride aerosols.

We divided the last termination into 4 stages by focusing on the temperature; Holocene, Younger Dryas (YD), Bolling-Allerød (B-A) and Last Glacial Period (LGP), and compared the mass ratio of sulfate and chloride aerosols in each stage. During the cold stage in YD and LGP, CaSO4 accounted large percentage of sulfate aerosols. On the other hand, during the warm stage in Holocene, Na2SO4 accounted large percentage of sulfate aerosols. In B-A, percentage of Na2SO4 is almost as same as that of CaSO4. Since CaSO4 is considered to be formed at first among sulfate salts in the atmosphere, these results are probably controlled by Ca2+ concentration. Mass ratio of NaCl/Na2SO4 decreased from LGP to Holocene (Fig. 2f), which indicate that sulfatization of NaCl increased toward Holocene.

Geochemistry and Petrology of the Timar basaltic volcanism in the northeast of Lake Van

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Timar Pliocene basaltic volcanism in the northeast of the Lake Van Basin erupted from local central eruption centers. Products of basaltic volcanism in the Timar region are covered by younger lavas of Late Pliocene Etrüsk volcanics and Quaternary basalts in age. Available K-Ar ages [1] indicate that basaltic volcanism observed in north and southeast of the Etrüsk volcano erupted in a period between 4.90 and 4.50 Ma corresponding to Zanclean (Pliocene). Alkaline-subalkaline basalts and hawaiites consist of olivine, augite, titanoaugite and plagioclase phenocrysts and micro-phenocrystals. The groundmass of these lavas contains the microcrystals of the same mineral assemblages and volcanic glass. They display porphyritic, glomeroporphyritic, intersertal and hyalopilitic textures.

Results of our FC, AFC and EC-AFC modelings indicate that the Timar basaltic lavas were slightly influenced by crustal contamination and fractional crystallization. MORB patterns of corrected data to MgO 9% show that some HFS elements such as Nb and Ta are depleted relative to LIL and LREE (La-Ce). This findings imply that Timar basaltic volcanism could have been derived from a mantle source with a distinct subduction component.

Results of our melting models indicate that the Timar basaltic rocks were derived from both shallow and deep mantle sources with different melting degrees ranging between 0.8 - 5 %. The percentage of spinel seems to have increased in the lerzolitic mantle source of the basaltic lavas. Accordingly, chemical character of the lavas turned from alkaline to subalkaline in time. We argue that the temporal increase of spinel contribution and the melting degree in the mantle source region was responsible for transition from alkaline to subalkaline character in the lava chemistry in time.


Conditions for Proterozoic anoxic and non-sulfidic ocean: Constraints from a marine biogeochemical cycle model

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Understanding the Earth’s oceanic redox evolution in response to several environmental conditions is one of the fundamental topics in the Earth science. Accumulating geochemical records, such as iron speciation and molybdenum geochemistry, reveal large spatial heterogeneity of Proterozoic ocean redox chemistry; anoxic and non-sulfidic (i.e., ferruginous) conditions had been prevailed throughout the Proterozoic, and sulfidic conditions might have covered only a small portion of the seafloor. However, the atmospheric oxygen level ($p_{O_2}$) in the Proterozoic has not been well constrained, and it remains unclear exactly what biogeochemical conditions are necessary to explain such redox structure in the Proterozoic ocean interior.

Here, we try to constrain the conditions for Proterozoic ocean redox structures by use of a marine biogeochemical cycle model in which C-N-P-O-S coupled biogeochemical cycles are taken into account. The results of systematic sensitivity experiments regarding $p_{O_2}$ and chemical weathering rate on land demonstrate that the conditions for pervasive euxinia are very limited, and widespread ferruginous condition would be an inevitable consequence of low $p_{O_2}$ and high pyrite burial efficiency during the Precambrian. Sulfidic waters would be restricted in near-shore regions where riverine sulfate flux is sufficient to stimulate the sulfate reduction. We also found that other environmental factors affecting long-term oceanic redox state (e.g., sea-level stand, settling rate of marine snow in water column) do not change above biogeochemical consequences.

These quantitative results would provide insight into further understanding of the Earth’s redox history and its stabilization mechanism(s) from a perspective of the biogeochemical dynamics. We also propose that shelf euxinia still has a significant impact on the availability of redox-sensitive, bioessential trace metals, and therefore would provide a linkage between evolution of ocean oxidation state and biological innovation.
Igneous and impact processes on a ureilite parent body inferred from Y-983890 polymict ureilite

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Ureilite is the second largest group of achondrites. They are largely divided into two types: monomict and polymict. Most ureilites are monomict ureilites, whereas polymict ureilites are relatively rare. Polymict ureilites are polymict breccias containing lithic clasts and mineral fragments of various lithologies [1]. Therefore, it provides valuable information about igneous and collisional processes on ureilite parent bodies. Yamato (Y-) 983890 is a recently classified new polymict ureilite [2]. In this study, we conducted careful petrographic observations on this new polymict ureilite.

Y-983890 consists of lithic clasts and mineral fragments which show a large variety of lithologies. Most of them are monomict ureilite-like materials. They consist of coarse-grained (up to 1 mm) olivine and/or pyroxene (pigeonite, orthopyroxene, and minor augite) with interstitial dark carbonaceous materials and/or graphite. The chemical compositions and Fe/Mg-Fe/Mn relations of olivine and pyroxene are consistent with those of monomict ureilites [3].

Non-monomict ureilite-like materials include feldspathic clasts, dark clasts, a chondrule fragment, and others. We identified several distinct feldspathic clasts. They show different igneous textures and different chemical compositions of constituent minerals (feldspar and pyroxene). Some of the feldspathic clasts are considered to be basaltic counterparts complementary to monomict ureilites (ultramafic residues). The dark clasts consist of fine-grained phyllosilicate-rich matrices with variable amounts of opaque minerals such as magnetite and sulfides (pyrrhotite, pentlandite). These dark clasts mineralogically resemble the matrices of CI carbonaceous chondrites. A chondrule fragment was also identified. It shows a barred olivine chondrule texture. The chemical composition of the olivine is in the range of that of H chondrite. The dark clasts and the chondrule fragment are considered to be fragments of impactors collided with the parent body of Y-983890.


Organic geochemical characteristics of the coaly Miocene units in the Şahinali (Aydın) region, Büyükk Menderes Graben, Turkey

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In the Şahinali (Aydın-Turkey) region the Miocene units consist of conglomerate, coal, clayey coal, sandstone, siltstone, claystone, clayey limestone and silicilimestone. Total Organic Carbon (TOC) values in these units range between 0.11-38.13 %. Rock-Eval analyses on core samples with the highest TOC values give hydrogen index (HI) values from 60-566 mgHC/gTOC and oxygen index (OI) values from 31-245 mgCO2/gTOC. The organic matter can be classified as Type II and III kerogen on the modified van Krevelen diagram. Tmax values vary between 338 and 429 °C, with an average of 413 °C indicating the diagenesis stage. Based on the microscopic studies, organic matter is composed of predominantly autochthonous algal and amorphous material, with a minor contribution of terrestrial material. The average vitrinite reflectance value is 0.35 %. Vitrinite reflection index and Tmax values indicate that the organic matter is immature. Biomarker characteristics also verify these results. 8t(H)-22, 29, 30-trisnorhopane Ts/(Ts+Tm) ratio is 0.85. This value indicates immature (Ts/Tm>1) organic matter, while C32 22S/(22S+22R) ratio is determined to be 2.56. Diasterane/sterane ratio is generally low in immature sediments - between 0.08-0.71 in the samples- in spite of the lithology effect. The thermal process is evaluated through the biomarker data during the coalification, and the Diasterane/sterane ratio indicates immature (Ts/Tm>1) organic matter. The Diasterane/sterane ratio is generally low in immature sediments - between 0.08-0.71 in the samples- in spite of the lithology effect. The thermal process is evaluated through the biomarker data during the coalification, and the Diasterane/sterane ratio is generally low in immature sediments - between 0.08-0.71 in the samples- in spite of the lithology effect. The thermal process is evaluated through the biomarker data during the coalification, and the Diasterane/sterane ratio is generally low in immature sediments - between 0.08-0.71 in the samples- in spite of the lithology effect. The thermal process is evaluated through the biomarker data during the coalification, and the Diasterane/sterane ratio is generally low in immature sediments - between 0.08-0.71 in the samples- in spite of the lithology effect.

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Effect of Magma Mixing on the evolution of the intermediate members of Süphan Volcanics: Eastern Turkey.

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The Süphan stratovolcano, representing one of the major eruption centers of the post-collisional volcanism in eastern Anatolia, Turkey, consists of lava flows, domes and pyroclastics ranging in composition from basalts to rhyolites. Geochemical data reveal transitional mildly alkaline to calc-alkaline character for the eruptive products. Ar-Ar age data and published K-Ar data from different levels of the volcanostratigraphic succession yield a range of 0.76-0.06 Ma. Mineral chemistry and textures indicate that magma mixing played an important role on the chemical diversity of Süphan volcanics [1]. Intermediate members of the volcanism show a wide range of mineral compositions, for pyroxenes, olivine and plagioclase, that are intermediate between those of basalts and rhyolites. Mineral thermometry of these rocks also yields a wide range of temperatures intermediate between rhyolite (~750 °C) and basalt (~1100 °C). Geochemical modeling [2] of major element compositions suggests that relatively mafic (SiO2 ≤ 55 wt %) and SiO2 rich (SiO2>~65 wt %) members of the Süphan volcanics evolved at moderately hydrated (H2O=1 wt %) and QFM (quartz-fayalite-magnetite) conditions at 2-4 kbar pressure. On the other hand, most of the lavas with SiO2 contents between ~ 57 - ~65 wt % are products of isobaric-isenthalpic mixing of 70% basaltic trachyandesitic magma (at 1100 °C) and 30 % rhyolitic magma (at 900 °C) at a crustal pressure of 0.5 kbar.


Trace Elements in the Environment at the Site of probable Underground Building in the Nizhnekansky Rock Massif (Siberian Craton)

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Trace elements were investigated along with geological exploration of the rock massif for underground isolation of radioactive wastes. Perspective site of rock massif is mainly formed by archaean gneisses with dykes of gabbros or dolerites. Exploration methods included well boring up to 700 m in depth, hydrogeological pumping, geophysical and environmental surface researches etc. Bedrocks (205 samples), soil (50), subsoil (50), bottom sediments (25), and natural taiga’s vegetation (15) were sampled for environmental analysis. The samples were tested by atomic absorption spectroscopy (AAS), ICP MS and partially chemical methods.

Searching correlations between different environmental systems and spatial distribution we defined two main types of trace elements, that differ on its’ origin. The first type named as autochthonous originated from parent bedrock. The second type named as allochthonous derived to industrial emissions. In turn, both types are subdivided into some groups that are characterized by different conditions of migration and concentration.

Inert elements (Be, Ga, Mo) have approximately equal concentrations in all searched systems. Cerium and lithium form a group named immobile in bedrock, both two elements were detected only in bedrock. A more widespread group, passive migrating to soil, is characterized by largest concentrations in rocks. Ba, Co, Cu, La, Pb, Sc, Sn, Ti, Y, Yb, Zn form this group.

The group of elements active migrating to soil has two sources of its origin: autochthonous and allochthonous. These elements have the largest concentrations in soils. Autochthonous elements derived from bedrocks are Ag, B, Cr, Ge, Nb, Ni, V, Zr. The source of Mn, Sr, and P is a fly ash, emitted by power and heating plants of the Krasnoyarsk, situated about 60-80 km to southwest.

Only one element, cadmium, is accumulated in surface landscapes. It was found in vegetation and bottom sediments but never in bedrock and soils. It may be also the result of industrial emission.
Primordial noble gas in the Solar System

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The solar noble gases, especially their isotopic compositions, are crucial reference parameters in discussing planetary evolution. Either Solar wind noble gas (SW) or Q-component in primitive meteorites, both widely occurring in the early solar system with very uniform isotopic composition (except for Q-Ne), has been regarded to represent the primordial solar noble gases. Current conventional practice is to assume the SW noble gases as the proxy of the solar noble gas [e.g.1]. However, on the basis of noble gas isotopic systematics based on noble gas isotopic data in various planetary objects, Ozima et al [2] concluded that Q-noble gas represented the solar noble gas, from which SW-noble gas was fractionated (30.3‰/amu at mass number 16). Here, we propose a new noble gas isotopic reference parameters for the primordial solar system with special reference to the neon isotope in the Earth, and discuss their implications on the evolution of terrestrial planets.

The primordial 20Ne/22Ne value in the Earth is still an enigma, but a common assumption is to assign the SW ratio of 20Ne/22Ne = 13.8 [e.g.1]. However, we infer from the above noble gas systematics [2] that 20Ne/22Ne in Q-noble gas, namely the solar 20Ne/22Ne, was close to 13.0. The ratio is almost identical with the in-situ observed ratio in the Jovian atmosphere [4], a likely locale for the primordial noble gas in the early solar system. Moreover, recent Ne isotopic ratios deduced from some mantle-derived materials such as basaltic glasses from Iceland [1] and Devonian plutonic rocks [5] showed the indigenous mantle component of 20Ne/22Ne = 13.0. The result would require revision of some of widely held Earth evolution models based on the conventional noble gas reference.

The geochemical evolution of lateral and vertical direction of Delihalil volcano (Yumurtalık, Turkey)

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The study area, located between Ceyhan and Osmaniye in Southern Turkey, is surrounded by pyroclastics and lavas of Delihalil volcano. The lateral and vertical composition of these lavas are different. Basaltic lavas have different shapes as porous and massive in this region. Generally, porous basalt is seen on surface. Geochemical evolution of the Delihalil basaltic volcanism in the vertical direction was investigated in this study.

Delihalil volcano and other young volcanics in study region erupted from late Pliocene to historical time along the NE-SW trending left lateral Yumurtalık fault zone in southern Turkey which is characterized by alkali olivine basalts on surface [1]. These lavas were drilled up to 20 m depth at different points. Core samples were taken to determine the vertical composition of lavas.

These lavas are composed of olivine, plagioclase, augite and titanomagnetite crystals and display porphyritic to aphyric textures. The basaltic lavas display transitional characteristics from alkaline to subalkaline and are basanite, alkali basalt and subalkaline basalt. MORB pattern of the basaltic lavas imply that basanitic and basaltic lavas erupted from Delihalil volcano could have been derived from a mantle source like within plate. LREE of the most primitive lavas display strong enrichments relative to HREE and MREE on Chondrite-normalized spider diagrams. This finding indicates the presence of garnet in the mantle source.

A partial melting model was conducted to evaluate partial melting processes in mantle source of the basanites and basalts in the Delihalil volcano alkaline volcanism. Results of this study suggest the presence of both strongly garnet and slightly spinel peridotite in the source, a partial melting degree of 0.1-3% and mixing of the derivative melts from them in the genesis of the mafic basanitic and basaltic lavas.