

## Toward a unified method for the quantification of volatiles in magmas via FTIR

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Fourier Transform Infrared (FTIR) spectroscopy is a common tool used to quantify dissolved volatiles in melts. The use of this method for the analysis of melt inclusions in particular is crucial to understanding a multitude of volcanic and geochemical processes such as magma storage, crystallization, and degassing. Despite the ubiquitous nature of this technique in the literature, standard methods for the retrieval of dissolved volatile concentrations from IR spectral data are poorly defined and often rely on hand-drawn or assumed straight-line-fit background curves that introduce significant error and variation within data sets. Propogated errors from differences in “acceptable” background curves for a single IR spectrum drawn by a set of individuals (or even by a single individual at different times) can equate to variation in final retrieved volatile concentrations on the order of wt%. In an effort to reconcile this problem, we are developing a simple software package capable of retrieving dissolved volatile concentrations (i.e. H<sub>2</sub>O, OH, CO<sub>2</sub>, and CO<sub>3</sub>) from FTIR spectra based on a set of standard peak fitting algorithms. By using spectroscopic first principles to define a volatile-free background spectra, peak heights, and ultimately volatile concentrations, we can eliminate variations between individual researchers that stem from the subjectivity in choosing a “good” background spectrum. In addition, the automation of this procedure by computer eliminates internal variation within data sets and expedites the process of analyzing large data sets.

Our software tool, currently in the early stages of development, will allow for the creation of volatile-free background spectra based on a curve fit to the user-input FTIR data. Subsequently, a calculation of peak heights and ultimately volatile concentrations (based on the Beer-Lambert law, given sample thickness, density, and absorption coefficient) can be performed. Our goal is to make the tool as transparent as possible in order that the user has more control over and understanding of the data transformations being performed. The program, written in Python and released under the Gnu Public License (GPLv3), is currently in alpha. We are now seeking input on the overall design, desired features, and back-end theory/computation.

## REE content of phosphogypsum from Romania

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Phosphogypsum is a technogenic product remaining after the extraction of phosphoric acid from raw phosphate, mainly apatite. The original phosphate rock contains large amounts of REE, mainly replacing Ca from apatite or included in other phosphate structures. About 70% of the REE contents are stacked in the phosphogypsum obtained after sulfuric attack of the raw phosphate and much less in the case of hydrochloric attack. In Romania, the sulfuric attack through the hemidihydrate (HDH) or dihydrate (DH) procedures was extensively used to obtain phosphoric acid at Turnu Măgurele (TM), Valea Călugărească (VC), Năvodari (N) and Bacău (B).

Inductively coupled plasma - atomic emission spectrometry (ICP-AES) analyses performed on selected samples of phosphogypsum from the four deposits showed that the contents in the main REE (cerium, erbium, neodymium, thorium, ytterbium) are specific for the phosphogypsum issued from the processing of sedimentary raw phosphates. The contents are given in the table.

Occ.	Ce (ppm)	Er (ppm)	La (ppm)	Nd (ppm)	Th (ppm)	Yb (ppm)
TM	29,1 - 663,1	0,9 - 11,7	22,7 - 469,0	21,1 - 260,5	0,3 - 20,8	1,1 - 6,8
VC	30,2 - 454,2	0,8 - 7,3	35,7 - 322,5	22,3 - 188,2	0,0 - 12,8	1,6 - 5,0
N	3,9 - 165,0	1,8 - 7,7	14,5 - 135,6	3,8 - 90,6	0,8 - 6,5	1,8 - 6,1
B	19,3 - 174,8	13,1 - 18,8	36,2 - 134,2	24,5 - 104,5	1,7 - 5,2	1,9 - 6,6

## Observation of geoneutrinos in Borexino

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Geoneutrinos are electron anti-neutrinos produced by long-lived radioactive isotopes in the earth's crust and mantle. Geoneutrinos can be detected in kton scale organic liquid scintillator detectors located in underground laboratories. The detection reaction being the inverse-beta decay which has a prompt and delayed signal. These signals are correlated in space and time. The anti-neutrino interacts with a proton from an hydrogen atom and will make a positron plus a neutron. The positron will promptly annihilate; the neutron will thermalize and be captured on hydrogen in some 250  $\mu$ s. In spite of the strong signature geoneutrino can only be detected in massive low background set-ups designed for low energy (1 MeV) neutrinos. Borexino at the Gran Sasso underground laboratory in Italy has been in operation since 2007 to search for sub-MeV solar neutrinos. The sun is a huge source of electron neutrinos. Observation of solar neutrinos provides a unique tool to study the interior of the sun. At present experimental studies of geoneutrinos are carried out with KamLAND at the Kamioka mine in Japan and with Borexino at Gran Sasso. The first attempt of a geoneutrino measurement was done in KamLAND in 2005. Only in 2010 and 2011 both Borexino and KamLAND observed at more the 4 $\sigma$  C.L. a signal from geoneutrinos. The search of geoneutrinos likewise the one of solar neutrinos for the sun provides a unique tool to probe the interior of the earth. Uranium and thorium from the crust and the mantle make the geoneutrino flux on surface. The energy spectrum of the detected geoneutrinos depends on the abundance of uranium and thorium and on the different beta decays in the two radioactive chains. A spectroscopy determination of the geoneutrino signal can be done. This has been recently shown by Borexino. By means of this analysis the ultimate goal of the geoneutrino search will be the determination of the uranium and thorium content in the mantle. For this purpose a combined analysis of more than one experiment results will be necessary. In this talk we will review the present status of geoneutrino research. We elaborate on the recent results from Borexino and KamLAND. The experimental difficulties and background sources will be discussed.

## Influence of osteopontin on apatite formation

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The classical crystallization theories have been shown to be incomplete, particularly in the field biomineralization where non-classical crystallization pathways are widespread [1], including prenucleation clusters in solution as known in CaCO<sub>3</sub> and calcium phosphates [2-4]. The picture is even more complicated when additives are also considered. For calcium phosphate biomineralization in vertebrates, phosphate-rich proteins are known to be important. Herein we show how one of these, the calcium binding phosphoprotein osteopontin, drastically modifies the prenucleation behavior during calcium phosphate formation.

The formation of calcium phosphate was investigated by constant pH (8.0) titration of dilute calcium chloride into a sodium phosphate solution [2]. The calcium activity was measured *in situ* using a calcium sensitive electrode. In the osteopontin-free case, the calcium activity is lower than the added amount reflecting the formation of a bound prenucleation state [2-4]. As the supersaturation increases, an amorphous intermediate is formed which transforms into crystalline apatite upon continued titration. When introducing osteopontin an additional intermediate is observed that remains in dispersion. Both intermediates were stabilized by osteopontin in a dose dependent manner. However, osteopontin did not significantly affect the prenucleation behaviour prior to the formation of the first intermediate.

The initial amorphous phase was HPO<sub>4</sub><sup>2-</sup>-rich. As more calcium was added, the stoichiometry gradually changed towards stoichiometric amorphous calcium phosphate (ACP), with a distinct increase in the PO<sub>4</sub><sup>3-</sup>/HPO<sub>4</sub><sup>2-</sup> ratio at the transition from intermediate 1 to 2. The final apatitic phase was also found to be calcium deficient.

For carbonates, multiple amorphous forms are known, which might influence what polymorph is formed [2]. The observed additive-stabilization of ACP could help unravel the role of additives in biomineral formation, including polymorph selection.

[1] Gower (2008) *Chem. Rev.* **108**, 4551-4627. [2] Gebauer *et al.* (2008) *Science* **322**, 1819-1822. [3] Dey *et al.* (2010) *Nat. Mater.* **9**, 1010-1014. [4] Habraken *et al.* (2013) *Nat Commun.* **4**, 1507

## Titanite from the Fish Canyon Tuff: Searching for clues to pre-eruptive magma chamber processes

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Magma-mixing is thought to be an important mechanism for initiating large-scale pyroclastic eruptions, and as such, may play a key role in the petrogenetic history of such eruptions. However, the fragmental and often glassy nature of pyroclastic deposits, and to some extent the homogenisation associated with emplacement at the surface, may act to mask the details of plutonic level petrogenesis. The deposits rarely display visible evidence of pre-eruptive mixing, and unless there is textural or geochemical alteration of phenocrysts prior to eruption, then evidence of mixing at depth may be very sparse.

Titanite is a geochemically robust accessory mineral that has the ability to serve as a sink for trace elements; the REE and HFSE in particular. Recently, it has been shown that compositional zoning of titanite from plutonic rocks can preserve a record of the changing conditions within a magma chamber, including evidence of magma-mixing processes [1].

This study aims to assess the ability of titanite found in volcanic rocks to preserve evidence of pre-eruptive petrogenetic processes, by conducting a coupled micro-textural and geochemical analysis of titanite from the Fish Canyon Tuff, Colorado, USA. It is thought that thermal rejuvenation of the silicic magma, caused by intrusion of mafic magma at the base of the magma chamber just prior to eruption of the tuff, served as a trigger for eruption [2]. Such an input of mafic magma could induce compositional, temperature, and oxygen fugacity changes in the chamber, to which titanite could respond

Preliminary results, from this ongoing study, show titanite to have compositional zoning with cores preferentially enriched in heavy REE and rims preferentially enriched in light REE; a reflection of the changing composition of the melt. Dissolution surfaces with inclusions of ilmenite are common, and provide evidence of changing titanite/ilmenite stability; interpreted here to reflect changes in oxygen fugacity brought about by replenishment of the chamber with fresh mafic magma.

[1] McLeod *et al.* (2011) *Journal of Petrology* **52**, 55-82. [2] Bachmann & Bergantz (2003) *Geology* **31**, 789-792.

## Molecular and Micro Element Remote Analysis of Leaves of the Green Plants

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Condition of the vegetative ground cover is an important determinant of environmental health. The global scale of this object requires using distant, primarily optical research techniques [1].

In particular, this may be done by measuring the fluorescence spectra and laser plasma emission during leaves surfaces ablation, which allows drawing certain conclusions about the state of photosynthetic apparatus and plant vegetation conditions [2].

This study was carried out by way of remote and laboratory tests, focused on research of fluorescence spectra in photosynthetic apparatus and plasma of green plants optical-induced breakdown under femtosecond laser radiation. Radiation wavelength of 650 ÷ 950 nm, pulse energy up to 10 mJ, length 50 ÷ 100 fs [3].

Chlorophyll fluorescence and absorption bands in the light-collecting antenna as well as the leaf reaction center with the range of 660 ÷ 800 nm were measured in the radiation spectra. The researched parameters helped to evaluate the current condition of plants photosynthetic apparatus.

Measurements of leaves micro element composition allow finding possible reasons which modify this condition.

Spectra of plasma emission from plant leaves located at 10 meter distance revealed the presence of sensitive spectral lines of atoms and ions of carbon, magnesium, iron, calcium, calcium, and copper. Lines of OH, Swan (C<sub>2</sub>), and Cyanogen (CN) were also observed in these spectra.

[1] Ageev B.G., *et al.* // Atmospheric and Oceanic Optics. 2007. **V.20**, No.01. P. 82-86. [2] Krivonosenko A.V., *et al.* // Atmospheric and Oceanic Optics. 2012. **V.25**, No.03. P. 268-272. [3] Afonosenko A.V., *et al.* // Atmospheric and Oceanic Optics. 2012. **V.25**, No.03. P. 237-243.

## Veined quartz of the Urals: Structure, mineralogy

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There are three major groups of the Ural quartz deposits: the Subpolar Urals group, the Middle Urals group and the South Urals one. The Subpolar group is represented by the typical hydrothermal veined deposits. Zhelannoe - one of the big Subpolar quartz deposit is described. It is located in monomineralic quartz sandstone. The quartz vein may be to 100 meters thick. Rutile, tourmaline, zircon and sericite are the major accessory minerals. The chief deleterious constituent in quartz is water, which is located in gas-liquid inclusions. The effective method for H<sub>2</sub>O elimination is described. High quality quartz glass may be produced after primary quartz enriching.

The Middle Urals is represented by two giant quartz deposits: Gora Khrustal'naya and Svetlaya Rechka. Gora Khrustal'naya is represented by one quartz body which size is 380X140X160 m. The content of quartz in this body is 98.89%. Quartz deposit was formed on the big massive of quartz-diorite and granite contact. The main accessory minerals are microcline, muscovite, kaolin, hydrogoethite and pyrite. Quartz has giant crystalline structure. The specific enriching technology is described for this quartz deposit.

The South Ural group of quartz deposits is represented by quartz veins disposed in East part of the Ufaleisky gneiss-migmatite complex. Length of quartz vein area is 50 km. There are more than 3000 quartz veins on this area. Granulated quartz is prevalent for this group of deposits. Field spars, micas, rutile, sphene, ilmenite and carbonates are the main accessory minerals. Concentration of impurities in granulated quartz is as the IOTA STD. There is standard technology of quartz enriching for these deposits.

One more type of quartz deposits associated with small Naily gold deposit is vein Tolstikha. It is situated 35 km north from Miass and localized at the contact of small gabbro pluton with the large Talovskii massif of serpentized dunites, peridotites, and pyroxenites. This is a new economic quartz object. To date, the gold deposit has been mined. The vein is 1000 m along the strike, up to 50 m wide, and is traced up to 450 m deep.

## Biogeochemistry of the deep mud-volcano biosphere in the Kumano forearc basin of the Nankai Trough

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Submarine mud-volcanoes are formed by the vertical intrusion of a lower density and deformable materials from deep realm to the seabed. The mud-volcanism transports deep-sourced fluids, elements and hydrocarbons to the seafloor, of which seepages support chemosynthetic benthic life, including microbial communities that mediate anaerobic oxidation of methane with sulfate reduction. However, biogeochemical and microbiological characteristics of the deep realm of submarine mud-volcano have remained largely unknown.

In 2009 and 2012, using the deep-sea drilling vessel *Chikyu*, we drilled one of the most active submarine mud-volcanoes in the Kumano forearc basin of the Nankai Trough, off the Kii Peninsula of Japan, down to 200 meters from the summit (33°67.581N, 136°56.8085E: 1,986.7 m in water depth). Cell count and molecular analysis indicate the presence of relatively small microbial communities (less than 10<sup>5</sup> cells/cm<sup>3</sup>) throughout the cored depth. Carbon isotopic compositions of bicarbonate and acetate in the pore water were found to be highly enriched in <sup>13</sup>C. High concentrations of hydrogen were also observed, indicating a thermodynamically preferential condition for microbial acetogenesis via CO<sub>2</sub> reduction (i.e., homo-acetogenesis) rather. Radiotracer incubation experiments showed that activities of homo-acetogenesis were 2-3 orders of magnitude higher than those of homo- and acetoclastic methanogenesis.

Consequently, our accumulative biogeochemical and microbiological data indicate that the deep biosphere in the submarine mud-volcano of the Nankai Trough accretionary wedge is characterized by tectonic and sedimentological regimes, and hence different from the previously explored subseafloor biosphere in stratified sediment on the continental margins.

## Exploration of the deep coalbed biosphere (IODP Expedition 337)

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Integrated Ocean Drilling Program (IODP) Expedition 337 was the first expedition dedicated to seafloor microbiology that used riser drilling technology [1]. IODP drill Site C0020 is located in a forearc basin formed by the subduction of the Pacific plate off the Shimokita Peninsula at a water depth of 1,180 m. Seismic profiles suggested the presence of deep, coal-bearing horizons at ~2 km seafloor depth. Our primary objectives during Expedition 337 were to study the relationship between the deep microbial biosphere and the seafloor coalbed and to explore the limits of life in horizons deeper than ever probed before by scientific ocean drilling. Among the questions that guided our research strategy was: Do deeply buried hydrocarbon reservoirs such as coalbeds act as geobiological reactors that sustain subsurface life by releasing nutrients and carbon substrates? To address this question and other objectives, we penetrated a 2,466 m deep sedimentary sequence with a series of coal layers at ~2 km below the seafloor. Hole C0020A is currently the deepest hole in the history of scientific ocean drilling [1].

During Expedition 337, over 1,700 microbiological and biogeochemical samples have successfully been obtained, for which rigorous contamination controls enable differentiation of contaminants from indigenous microbial communities. We conducted gas chemistry and isotopic analyses using a new mud-gas monitoring laboratory during riser-drilling operation [1], which provided the first indication of biologically mediated CO<sub>2</sub> reduction to methane at the 2 km-deep coalbed layers. The numbers of microbial cells are generally less than 10<sup>3</sup> cells cm<sup>-3</sup>; however, increase of biomass was observed at the coal layers. Potential rates of organoclastic sulfate reduction are elevated in coalbed-bearing strata.

[1] Inagaki, Hinrichs, Kubo and Expedition 337 Scientists. *IODP Prel. Rept.*, 337 (2012).

## Studies on the concentration of I-129 and I-131/I-129 ratios in soil samples collected from Fukushima Prefecture

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A large amount of I-131 was released from the Fukushima nuclear power plant accident. Radioiodine accumulates in thyroid gland and radiation risk would be enhanced. Therefore, it is necessary to obtain deposition date of I-131 in Fukushima Prefecture. Because of the short half-life of I-131 (8 days), it was below the detection limit after a few months. On the other hand, I-129 released simultaneously with I-131 still remained in soil, due to its long half-life of 1.57×10<sup>7</sup> years. Therefore, I-129 can be used in the estimation of the I-131 deposition. For this purpose, it is essential to obtain I-131/I-129 ratios for calculating the amount of I-131 deposition from the I-129 analysis.

We used Fukushima soil samples in which I-131 had been measured. Iodine was separated by pyrohydrolysis and the evaporated iodine was collected in a trap solution. Stable iodine (I-127) concentrations in the trap solution were measured by ICP-MS. Solvent extraction was performed, and iodine was purified. Silver nitrate was added to precipitate AgI as a target for AMS and the I-129/I-127 ratios were measured by AMS at MALT, the University of Tokyo. For the estimation of I-129 concentrations (Bq/kg) the I-129/I-127 ratios and I-127 concentrations were used.

We obtained concentration (Bq/kg) of I-129 in soil and deposition density (Bq/m<sup>2</sup>) for more than 100 samples collected from different locations in Fukushima. It is interesting to note that a good correlation was found between the concentrations of I-131 and I-129 in soil samples. This finding suggests the possibility to estimate I-131 levels in soil at the early stage of the accident through the analysis of I-129. We obtained an average I-131/I-129 ratio as (2.1 ± 0.7) × 10<sup>7</sup>, although these are still uncertainties.

We also studied the concentrations of I-129 according to the soil depth. Compared to the depth profile of radiocesium, radioiodine was found to migrate faster into the deeper soil layer.

## Mechanisms and kinetics of hydrogen exchange in olivine: A review from experimental and computational studies

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Mobility of hydrogen in mantle minerals and especially olivine has raised interest for its impact on mantle properties for many years. Nevertheless, the mechanisms and kinetics of hydrogen exchange in olivine remain largely misunderstood. We present here a review on the current knowledge of hydrogen kinetics in olivine, highlighted by recent results from experiments [1], [2] and numerical modelling [3]. In forsterite, laboratory's experiments, suggest that incorporation of hydrogen is controlled by the mobility of magnesium vacancies with a diffusion of hydrogen faster than exchange rate along direction [100] and slower in the two other directions. A common kinetics is generally observed for all OH bands, in apparent contradiction with their different origin as highlighted by numerical modelling. In olivine, diffusion of small-polarons is faster than diffusion of hydrogen. These results suggest that diffusion of polarons is anisotropic, with diffusion along [100] probably faster. Theoretical interpretations in connexion with electrical conductivity properties of olivine are discussed.

[1] Du Frane and Tyburczy (2012) *Geochem Geophys Geosyst* DOI:10.1029/2011GC003895. [2] Ingrin *et al.* (2013) *Phys Chem Mineral* DOI: 10.1007/s00269-013-0587-3. [3] Balan *et al.* (2011) *Eur J Mineral* DOI: 10.1127/0935-1221/2011/0023-2090.

## The nitrogen isotope composition of volcanic fluids

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The main potential sources of nitrogen in volcanic and hydrothermal fluids are (i) the atmosphere; (ii) the upper mantle, including contribution from the subducting plates at the arc settings; (iii) the lower mantle at the hot spot settings; and (iv) the continental crust. The meaningful differences in  $\delta^{15}\text{N}$  among the four main potential sources of nitrogen make it a useful tracer providing relevant information on the geodynamic environments in which volcanic fluids are generated.

Here we present a large and new data set of nitrogen isotope,  $\text{N}_2/^{36}\text{Ar}$  and  $^3\text{He}/^4\text{He}$  in fluids from more of 20 volcanic systems of different geodynamic setting including subduction zones (Mediterranean volcanoes, Mexico, Central and South America, Kamchatka); spreading zones (Socorro Island) and hotspots (Iceland, Azores, Galapagos). The goals of this work are i) to identify the relationships between the geodynamic setting and the isotopic composition of nitrogen in volcanic fluids; ii) to characterize the lower mantle (fluids with  $^3\text{He}/^4\text{He}$  much higher than MORB values) in terms of  $\delta^{15}\text{N}$  and iii) to understand the inhomogeneity of  $\delta^{15}\text{N}$  with respect to the upper mantle.

The preliminary obtained results showed a wide range of  $\delta^{15}\text{N}$  values, for estimated deep component (ASW corrected), from +7 to -16‰. The fluids related to subduction zones are characterized by values from -5‰ to +7‰, while the very light  $\delta^{15}\text{N}$  (up to -16‰), were found in some gases of Iceland evidencing an important contribution from the lower mantle. We also discuss some problems related to possible effects of the nitrogen isotope fractionation ( $\text{N}_2\text{-NH}_3$  system) and to the air correction procedure.

## Experimental studies of catalytic properties of Iron II and III modified hydrothermal zeolites

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Zeolites are natural minerals formed by condensation of silica, alumina and some metallic hydroxides under hydrothermal systems [1], known by their porous structure and remarkable catalytic properties related to their high surface area, among others characteristics. Moreover, they present high affinity to absorb gases in their crystalline structure (i.e., H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>), decreasing their activation energy barrier promoting recombination of between them [2]. They may occur in hydrothermal systems where constant emission of hydrogen as a product of weathering of the marine lithosphere can react with the dissolved gases in seawater [3]. Hydrothermal systems are considered present since the Hadean when the Earth's seas had formed. Therefore, the interaction of minerals could enhance the nitrogen reduction as well as its subsequent recombination into larger organics [4].

We present results of enhancement of the surface area, porosity properties, and acidity of two synthetic iron II and III zeolites and a feldspar - analcime, phillipsite, sanidine - in comparison to the native mineral. These metallic inclusions in the zeolite structure provoke an enlargement of the internal channels and cavities, as well as creating Brønsted acid sites responsible of a stronger adsorption of N<sub>2</sub> o CO<sub>2</sub>.

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## Balance of carbon in the system of geochemically linked mire landscapes

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According to V.I. Vernadskiy, migration of chemical elements in biosphere is carried out at direct participation of biogenic matter. The purpose of long-term researches (1996-2011 ye) was studying balance of carbon in bogs. As modeling object for researches it was accepted on territory of Vasyugan mire spurs (West Siberia).

Investigations have shown, that peat deposits of oligotrophic mires are biochemical active on all structure and the dynamic of biochemical processes is determined by hydrothermal conditions. Process of organic matter transformation in a peat deposit and formations CO<sub>2</sub> is determined by temperature of peatland. The greatest concentration of methane in a peat deposit is marked in damp years. As a result of this processes was confirmed with long-term dynamics of gas structure («peepers»-method), carbon balance oligotrophic mires on territory of Vasyugan mire spurs has the following kind.

Position on Landscapes mires	Receipt of carbon,	Allocation of carbon,	Deposition of carbon,
	gC/m <sup>2</sup> *year		
Trans accumulative	267.3	97.6	169.7
Transit	235.2	66.9	168.3
Autonomy	158.0	65.2	92.8
<b>Average</b>	<b>220.0</b>	<b>76.6</b>	<b>143.6</b>

**Table 1:** Carbon balance of Landscapes mires.

In balance of carbon article of the charge determining carrying out of carbon with a drain of mire waters has essential value. According to our results, the average contents of carbon in mire waters, including carbon humic acids, changes from 53 up to 92,5 mg/l with limits 27,8-145 mg/l.

In a result the special kind of mire waters is formed. On the basis of the mathematical model carrying out of organic carbon by mire waters was designed 6,9 g m<sup>2</sup>/m<sup>1</sup>. But, and in view of losses of carbon with a drain of mire waters, on oligotrophic mires deposition of carbon, and, hence, is observed peat formation process is progresses.

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## Geochemistry of uranium and thorium in soils on the Ditrău Alkaline Massif, Eastern Carpathians, Romania

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The rocks of the Ditrău Massif (syenite, nepheline syenite, hornblendite, diorite, monzonite, monzodiorite, granitoid) have naturally higher uranium and thorium contents, making the area ideal for the study of the distribution in soils of these elements. The soil types present in the investigated area, according to the Romanian Soil Taxonomic Classification are: lithosol, redzine, eutricambosol, districombosol, typical luvisol, albic luvisol, ethnic luvisol and aluviosols. Uranium and thorium were analyzed in 70 soil samples collected from an equable points net for all type of representative rocks. U and Th concentration were measured non-destructively using gamma-ray spectrometry with HPGe detector, and the uranium and thorium bearing minerals in soil samples were identified by XRD. The pH values were determined using a digital pH-meter.

U concentrations in the soil varies between 0.5 and 9.3  $\mu\text{g g}^{-1}$  (6.18-114.86 Bq/Kg) and Th concentrations from 2 to 51.3  $\mu\text{g g}^{-1}$  (8.12-208.28 Bq/Kg), whereas the Th/U ration in soil ranges from 1.87 to 19.52  $\mu\text{g g}^{-1}$ . The pH varies from 3.6 to 7.3 and it controls the distribution of uranium and thorium in soil. Unlike U which is a mobile element, soluble in the U<sup>+6</sup> state (oxidizing conditions), Th has low mobility under environmental conditions and reflects source area characteristics. XRD analysis enabled the identification of U and Th as major or trace elements in minerals like zircon, thorite, allanite, monazite, pyrochlore, aeschynite, columbite, bastnäsite. The distribution of U and Th in soils is primarily controlled by the distribution of the accessory minerals in bedrocks, and secondly by the physical and chemical stability of these minerals in the pedogenetic process. The soils developed on granitoid rocks that occur in the north-eastern and eastern parts of the massif have the highest thorium content among all types of soils. High uranium contents were determined in soil samples developed on syenite and nepheline syenite. A positive correlation between uranium and thorium occurs in almost all type of soils.

Also, the results indicate an U and Th enrichment in the clay fraction.

## The origin of garnet peridotites in the Siberian cratonic mantle from chemical, modal and textural data

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Garnet peridotites, the most common rocks in cratonic mantle, are believed to be variably enriched residues of high-degree melt extraction, but the role and conditions of melting, metasomatism and deformation in their origin continue to be debated. A major problem is that peridotite xenoliths in kimberlites are usually altered during and after their transport to the surface, many are small and heterogeneous. We examine new and published [1-3] chemical, modal and textural data on several dozen large, fresh and homogeneous garnet peridotite xenoliths from the Udachnaya kimberlite in the central Siberian craton to better constrain the origin and evolution of garnet-facies cratonic mantle.

The least metasomatized garnet peridotites are similar in major oxide compositions to low-opx spl harzburgites from Udachnaya (interpreted as pristine melt extraction residues [4]) and were formed by 30–38% of polybaric fractional melting from 7–4 GPa to  $\leq 1-3$  GPa. Their whole-rock (WR)  $\text{Al}_2\text{O}_3$  and Mg#, hence melt extraction degrees, do not vary with depth. Co-variations of modal abundances, major oxides and their ratios in WR indicate that garnet is mainly a residual mineral, which survived partial melting and/or exsolved from high-T opx on cooling, whereas cpx is mainly metasomatic. Modal abundances of garnet can be estimated from WR  $\text{Al}_2\text{O}_3$ ; rocks with  $\text{Cr}\#_{\text{WR}} > \text{Cr}\#_{\text{gar}}$  contain accessory Cr-spinel.

In addition to coarse and sheared peridotites, we identify “transitional” rocks with  $\leq 10\%$  neoblasts at margins of coarse olivine. Such incipient stages of deformation may have been overlooked in previous studies of altered xenoliths in the Siberian and other cratons. Regardless of deformation degrees deformed peridotites show stronger enrichments in Fe, Ti, Ca, REE than coarse peridotites, i.e. deformation is accompanied by metasomatism. Both deformed and coarse peridotites occur near the base of the lithosphere ( $\geq 1300^\circ\text{C}$ , 6.8 GPa). P-T estimates define a perturbed geotherm [3]; oxygen fugacity decreases with depth less than inferred previously [3, 5].

[1] Ionov *et al.* (2010) *J Petrol* **51**, 2177-2210. [2] Doucet *et al.* (2013) *CMP* **165** (6). [3] Goncharov *et al.* (2012) *EPSL* **357-358**, 99-110. [4] Doucet *et al.* (2012) *EPSL* **359-360**, 206-218. [5] Yaxley *et al.* (2012) *Lithos* **140-141**, 142-151.



## Arsenic contamination in an anoxic aquifer in southwest Germany: Assessment and process studies

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Arsenic groundwater contamination due to the infiltration of arsenic bearing sewage has been assessed analysing groundwater and aquifer material on an abandoned industrial site in the quaternary aquifer in the Upper Rhine Rift, southwest Germany. The contamination plume is about 800 m long, 200 m wide and 20-30 m deep. Detailed studies were performed in order to investigate the redox state and the binding forms of arsenic in the water and in the aquifer material, respectively.

A cross section of four liner boreholes along the plume was drilled and analysed in detail as well as 20 direct push soundings in the center of the contamination. Groundwater was sampled using filtered groundwater wells and the direct push boreholes. The analyses lead to a detailed assessment of the contamination extension and mass. This assessment could also be used to characterize the mobility of both arsenic redox species.

The transport processes in the aquifer were studied more in detail using column experiments with contaminated material under oxic and anoxic conditions. It could be shown that surface complexation and microbial redox processes dominantly influence the arsenic mobility under anoxic conditions. The reduction of As (V) to As (III) following iron reduction seems to be the dominating process under the aquifer conditions.

Similar processes have also been observed during field studies with As (V) input into the Cape Cod Aquifer [1]. Both sites are characterized by an iron dominated redox system. They are anoxic due to contamination with sewage of organic contaminants. The sites differ in the geochemical milieu; whereas the contaminated site in the Upper Rhine Valley is a carbonate system, the Cape Cod aquifer is acidic.

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[1] Höhn *et al.*, (2006): *J. Cont. Hydrology* **88**, 36-54

## U-Pb dating of Eoarchaeon zircons using a NanoSIMS

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Volatiles, such as hydrogen or sulphur, included in Eoarchaeon igneous rocks, have crucial information to reveal about the evolution of the early Earth. Apatite and/or glass inclusions, found in zircon crystals, are expected to preserve primitive information of such volatile elements. NanoSIMS is one of the more powerful tools for micro-scale analyses including precise *in situ* U-Pb dating of zircon.

We performed <sup>238</sup>U-<sup>206</sup>Pb and <sup>207</sup>Pb-<sup>206</sup>Pb zircon dating using a NanoSIMS 50 ion microprobe at the University of Tokyo, with the method developed by our group [1]. The targeted zircons were separated from a tonalite of the Eoarchaeon Nuvvuagittuq supracrustal belt, Superior Craton, Canada. The reported U-Pb age of this tonalite is 3661 ± 4 Ma [2]. Euhedral to subeuhedral zircon crystals were picked up. Some of them have a zoning structure. Glass or apatite inclusions, whose size were 10 to 30 micrometers in diameter, were found in the crystal.

After the correction of common lead, <sup>238</sup>U/<sup>206</sup>Pb\* and <sup>207</sup>Pb\*/<sup>206</sup>Pb\* ratios of 20 crystals were plotted on Terra-Wasserburg Concordia diagram. They showed a Discordia suggesting recent Pb loss. The intersection of Concordia and Discordia indicates that the age of this rock is 3637 ± 19 Ma, which agrees well with previous study. Now we are trying to measure the volatile compositions of inclusions in these zircons.

[1] Takahata *et al.*, *Gondwana Res.*, 14, 587-596, 2008. [2] David *et al.*, *GSA Bulletin*, 121, 150-163, 2008.

## Geo-neutrino measurements with KamLAND

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### KamLAND experiment

The Kamioka Liquid-scintillator Antineutrino Detector (KamLAND) is a 1 kton liquid scintillator surrounded by 53 nuclear reactor units in JAPAN. Following the Fukushima nuclear accident in March 2011, the entire Japanese nuclear industry, which generates > 97% of the reactor neutrino flux at KamLAND, has been subjected to a protracted shutdown. The reactor-off period provides a unique opportunity to measure geo-neutrino with KamLAND.

### Geo-neutrino analysis [1]

The data reported here are based on a total live-time of 2991 days, which includes the recent reactor-off period. Assuming a chondritic Th/U mass ratio, we obtain a geo-neutrino flux of  $3.4^{+0.8}_{-0.8} \times 10^6 \text{ cm}^{-2}\text{s}^{-1}$  from <sup>238</sup>U and <sup>232</sup>Th at the KamLAND location. The geo-neutrino flux translates to a total radiogenic heat production of  $11.2^{+7.9}_{-5.1}$  TW from <sup>238</sup>U and <sup>232</sup>Th. The flux estimation is significantly improved by the reactor-off data. The geodynamical prediction with the homogeneous hypothesis is disfavored at 89% C.L. (Fig. 1) The observed flux is in agreement with the predictions from existing BSE models (geodynamical [2], geochemical [3] and cosmochemical [4]) with in  $\sim 2\sigma$ .

### Future prospects

The ability of discriminating between models is limited by the statistical uncertainty. KamLAND continues to measure for getting further statistics. In the future, improved measurements with higher statistics and lower background is desired. Directional geo-neutrino detection is also required to further understand the deep interior of the Earth.

[1] A. Gando *et al.*, arXiv:1303.4667. [2] D. L. Turcotte and G. Schubert, *Geodynamics, Applications of Continuum Physics to Geological Problems*, second ed. (Cambridge Univ. Press, Cambridge, 2002). [3] W. F. McDonough and S.-s. Sun, *Chem. Geol.* 120, 223 (1995). [4] M. Javoy *et al.*, *Earth and Planet. Sci. Lett.* 293, 259 (2010).

## Natural analogue study on long term alteration of bentonite (1) - Geochemistry and clay mineralogy-

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In order to evaluate the long-term behavior of the bentonite in geological disposal sites for TRU waste, the prediction of alkaline alteration by cement influences is very important. We conducted geochemical analyses of natural bentonite suffered from Ca-rich groundwater as a natural analogue of bentonite barrier after  $\sim 100\text{kyr}$ .

The drilling survey was carried out on geothermal site at a Japanese island arc basin to find similar environment to the bentonite barrier influenced by cement leachates. The hot spring water near the site has high concentration of Ca and pH. We drilled down to GL-250 m, and the tuffaceous bed was recognized in the depth of GL-240m. The sedimentary age of the bed was estimated as 8.2 - 5.6 Ma by analysis of microfossils. Post-sedimental thermal history was estimated to be 20-40 degrees by analysis of stable isotopes. According to whole-rock XRF data, this bentonite could have been altered from basalt-dacite (granite) bimodal igneous rocks. Backscattered electron imaging on the bentonite identified coexisting Na/Ca-smectite and heulandite (Fig.1).

Even in such a Ca-rich condition, Na-smectite still remains without complete conversion to Ca-smectite. Geochronology by fission track dating and <sup>36</sup>Cl/Cl suggested about 10Ma for igneous age and 2Ma for groundwater entrapment. The composition of present groundwater was estimated as the mixture of rainwater and near hot spring water from a result of principal component analysis.

It is inferred that the Na-type smectite could have coexisted with the Ca-type in the bentonite for this geologic time-scale. This natural analogue may suggest a supporting evidence of smectite stability at the repository.

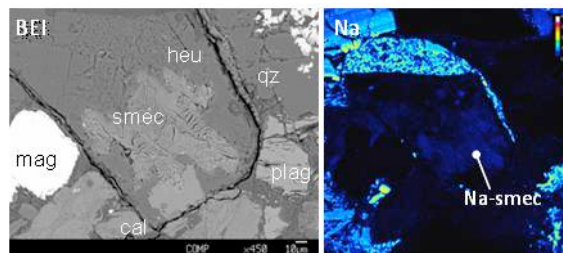


Fig.1 BEI and Na-map of the altered bentonite.

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## Re-evaluation of digestion methods for accurate Re-Os isotope and highly siderophile element analyses

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The current database on highly siderophile elements (HSEs: Re, Au, Ir, Os, Ru, Rh, Pt and Pd) and Os isotopes in geological samples is dominated by isotope dilution methods, coupled with high-temperature sample digestion using inverse aqua regia in closed glass vessels such as Carius tubes (CT) or a high-pressure asher system (HPA). These acid digestion techniques are preferred over traditional flux fusion techniques, such as NiS fire assay, largely due to the ability to measure Re and Os on the same sample aliquot. By contrast, two major limitations - the 'nugget effect' and incomplete digestion - have often been associated with these acid digestion techniques. Recent data suggest that an additional HF step is essential to release HSEs hosted in the silicate portions of certain basaltic materials, necessitating modification of typical digesting procedures.

To address this issue, we systematically conducted analytical tests for CANMET reference material TDB-1 with varying digestion apparatus (microwave, CT, HPA), conditions (temperature, duration, sample size) and protocol (with or without HF desilicification, either before or after aqua regia attack). We found the optimum method for simultaneous determination of <sup>187</sup>Os/<sup>188</sup>Os and HSE concentrations used inverse aqua regia to attack 1-2 g of powder over long durations, such as a Carius tube heated to 240°C for 72 hours, followed by an HF desilicification step after CCl<sub>4</sub> solvent extraction of Os. It is anticipated that extended HPA digestions will also achieve the same effect.

The method provides strong linear correlations on Os versus Ir-Ru-Pt concentration diagrams for repeat dissolutions of TDB-1, reflecting an effect of powder heterogeneity. This is further supported by a linear array on the <sup>187</sup>Re/<sup>188</sup>Os and <sup>187</sup>Os/<sup>188</sup>Os diagram, yielding a meaningful age of 1230 ± 47 Ma (MSWD=2.1), consistent with the Mesoproterozoic (~1265 Ma) formation of diabase TDB-1. In comparison, excellent reproducibilities for all HSEs were obtained from USGS reference material BIR-1: RSDs for 1-2 g aliquots were 7.4% Os, 4.4% Ir, 1.5% Ru, 5.2% Pt, 1.6% Pd and 0.7% Re (n=8). Thus, BIR-1 might be suitable material for narrowing the confidence intervals of HSE certified values.

## Metasomatism recorded in the peridotite overlying metamorphic sole of the the Oman ophiolite: an analog of mantle-wedge events

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Mantle peridotites have been modified to various extents at slab-mantle interface within the mantle wedge. To know the details of the event, e.g., which elements and how much amounts?, the materials from the mantle wedge are needed. Ophiolite is a place where we can investigate the slab-mantle interaction, because it has the metamorphic sole, formed at the ophiolite obduction. Its formation is interpreted as an analog of an incipient arc system transformed from the ocean floor.

The Oman ophiolite is quite famous for good exposure and preservation of the oceanic stratigraphy with widespread formation of metamorphic sole. We did systematic sampling at the southern Oman ophiolite from the sole garnet amphibolite to the peridotite up to 110 m above the amphibolite/peridotite boundary, i.e., an analog of slab-mantle boundary. The peridotite is deformed and serpentinized to various degree, and occasionally has mylonitized bands. The peridotite protolith is fertile lherzolite: the Fo content of olivine and Cr# [= Cr/ (Cr + Al) cation ratio] of chromian spinel is 90-93 and 0.11-0.35 (except for the spinels in highly serpentinized peridotite), respectively. The Al<sub>2</sub>O<sub>3</sub> contents of clinopyroxenes and orthopyroxenes are high (up to 5.3 and 6.3 wt.%, respectively). Fine pyroxene grains show a low Al<sub>2</sub>O<sub>3</sub> content, < 1 wt.%. The peridotites contain amphiboles irrespective of the distance from the amphibolite/peridotite boundary, and the amphiboles are not only tremolite after clinopyroxene but also hornblendes. The incompatible trace-element patterns of clinopyroxene are enriched in LREE and some LILE (Rb, Ba and Sr), and those of hornblendes show similar patterns although some show higher abundances than clinopyroxene.

The peridotites just above the metamorphic sole have been cooled as well as extensively hydrated (at least 110 m above the boundary) and enriched in fluid-mobile elements as mantle-wedge peridotites.

## REE signatures of accessory minerals from Iron Oxide Copper Gold - skarn mineralization, Hillside, South Australia

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Hillside is an Iron Oxide Copper Gold (IOCG) mineralized system in the Gawler Craton, typified by skarn associations and genetically tied to the ~1.59 Ga Hiltaba Intrusive Suite. Incorporation of REE in skarn and accessory minerals is a valuable tool for understanding evolution of REE-enriched IOCG deposits and their footprints.

Mineralization is hosted within calcic skarns comprising prograde garnet-pyroxene-magnetite and retrograde epidote-actinolite-hematite associations. Early, high-temperature (~750 °C; Zr-in-titanite geothermometry) pyroxene skarn (I) is tied to strong albitization. Pyrite, present in the calcic skarn (II), is replaced by chalcopyrite during the late-hydrothermal (main Cu-Au ore deposition, III) stage. Titanite, apatite and allanite are abundant throughout all stages of skarn evolution from early-prograde to late-hydrothermal collapse.

REE concentrations and distributions in skarn and accessory minerals were determined by LA-ICP-MS. Whereas skarn minerals are extensively replaced in the main ore stage, accessories are still present, and their REE trends depict all stages of evolution (Fig. 1). Significantly, they record HREE-enrichment in stage III. This can be interpreted as a response to change in the  $fS_2$  character of fluids.

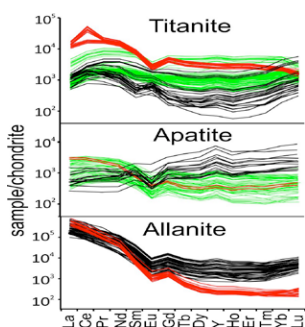


Figure 1 Chondrite-normalized REE+Y plots for accessory minerals. Red - early skarn (I); green - main calcic skarn (II); black - main sulfide deposition (III). Note progressive LREE-depletion and HREE-enrichment during evolution of the IOCG-skarn system.

The data show that REE signatures of accessory minerals from IOCG systems can help monitor development of alteration, and provide a framework for discriminating mineralized from non-mineralized systems in the region.

## Mid to Late Holocene decreasing precipitation trends as reflected in $\delta^{18}O$ of speleothems from Apuan Alps (central Italy): Implications for seasonality

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Changes in insolation related to Earth's orbital variations played a central role in the global-scale changes in climate of the last 11,500 cal yr. A progressive decline in summer temperature since the middle Holocene is well established from pollen and plant macrofossil data in northern and central Europe. The Mediterranean region has also become drier from the Middle Holocene to the present, with a marked precipitation seasonality that is crucial for both Mediterranean ecosystems and societies. Several records show contrasting seasonality patterns between southern and northern border regions of the central Mediterranean during Middle to Late Holocene. In this poster we present  $\delta^{18}O$  stalagmite data sets from Corchia and Renella caves (Central Italy), showing long-term trends of increasing values (i.e. reduced rainfall) from Middle to late Holocene, while at secular to millennial scale they present different behavior. This difference is due to the variable recharge conditions related to changes in seasonality. These data can provide a more precise picture of the variations in the seasonality in the Mediterranean area

## On the arrangement of sodium atoms around structural units and vibrational properties of a sodium borosilicate glass

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We have used first principles simulations in order to investigate the properties of a sodium borosilicate glass of composition  $3\text{Na}_2\text{O}-\text{B}_2\text{O}_3-6\text{SiO}_2$  (NBS). This composition is similar to that of the glass wool used in our daily life. The study was carried up using first principles molecular dynamics within the density functional theory framework as implemented in the VASP code [1].

In this talk, we will present the analysis of the local environments of the three building structural units of the glass network, namely silicon atoms in 4-fold coordination, and boron atoms with 3- or 4-fold coordination. We will also discuss the local distribution of the Na atoms around the basic structural units. Indeed we have identified their preferential neighborhoods and how the nature of network former and its coordination infer on the shape of these preferential regions of Na atoms.

The vibrational properties have been equally studied, and the contributions of the various species have been identified. We have found that 3- and 4-fold coordinated boron atoms give rise to distinguished spectral features. Moreover, the partial vibrational density of the 3-fold coordinated B atoms has been found to be a weighted sum of 2 specific contributions so-called 3-fold symmetric coordinated B atoms and asymmetric coordinated B atoms.

[1] Kresse & Hafner (1993) *PRB* **47**, 558; Kresse & Furthmüller (1996) *Comp.Mater. Sci.* **6**, 15; Kresse & Furthmüller (1996) *PRB* **54**, 1116

## Different diagenetic behaviors of As, Mo and Sb in Lake Biwa, Japan

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Lake Biwa, the biggest lake in Japan, is suitable field to study diagenetic behavior of redox sensitive oxyanions, since clear diagenetic accumulation of Mn and As in surface sediment have been observed from entire lake. Redox speciation of Mn and As determined by XANES, were significantly varied depending on the sampling location within the lake. Here we show the comparison of depth profile of As, Sb, and Mo in both solid phase and porewater among various redox conditions. Of the seven stations studied, As profiles in porewater showed clear concentration peak in six. The depth of these peaks ranged from 3 to 1 cm below sediment-water interface, and arsenite was the dominant species around the areas where the peaks appeared. The peak values of As in solid phase always appeared 1-2.5 cm above the places where the peaks of porewaters were found. Predominance of arsenate in surface sediments suggested diagenetic accumulation of As, whereas As-S species becomes predominant below As peak areas in porewater. Both Mo and Sb showed cocentration peak in 5 stations. Two stations in which the peaks were not observed are in areas with most reducing conditions where no  $\text{MnO}_2$  enrichment was observed even in the top layer (0-5 mm). In the other 5 stations, depth of the peaks in porewater were always in the following order:  $\text{As} > \text{Sb} > \text{Mo}$ . Difference in peak depth between As and other 2 elements were 0.75-1.5 cm, whereas difference between Sb and Mo were  $< 0.75$  cm. It is well known that these oxyanions have high affinity to Fe (oxy)hydroxides. However, if the dissolution of this phase predominantly controls the solid-water partitioning of these oxyanions, the porewater profile should be similar. Distinctly higher depth of As peak is likely attributed to arsenate reduction to arsenite which enhances the mobility of As. Slight differences in Mo and Sb is possibly due to high affinity of Mo to  $\text{MnO}_2$  that reduces more easily than Fe (oxy)hydroxides. Although these relative mobility should change in more sulfidic setting like seawater, such a comparison is rather limited in freshwater system so far, thereby the finding of this study can contribute for better understanding of diagenetic behavior of these elements.

## Role of acid mobilization in projected response of soluble iron supply to improvement of air quality in the future

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Acidification of dust aerosols may increase aerosol iron (Fe) solubility, which is linked to mineral properties (e.g., crystallinity, grain size and impurity content). The mixing of the mineral dust with combustion aerosols can also elevate iron solubility when aerosol loading is low. Here, we use a process-based chemical transport model [1, 2] with improved treatment of Fe in mineral dust and proton-promoted dissolution scheme to investigate the deposition of soluble iron and its response to changes in anthropogenic emissions of both primary particles and precursor gases.

Comparisons of modeled Fe dissolution curves with the measured dissolution rates show overall good agreement under acidic conditions. The improved treatment of Fe in mineral dust and the proton-promoted dissolution scheme results in reasonable predictive capability for iron solubility over the oceans in the Northern Hemisphere. Our model results suggest that iron included in aluminosilicate dust can be released in the form of ferrihydrite colloids, nanoparticles and aqueous species during the long-range transport and thus provide an important bioavailable source of iron to the oceans. As a result of considering both the atmospheric processing of mineral dust and source composition of combustion aerosols, soluble iron deposition to the subarctic North Pacific is projected to respond nonlinearly to changing emissions of fly ash and air pollutant gases (e.g., SO<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub>). These results could have important implications for iron fertilization of phytoplankton growth, and highlight the necessity of improving the process-based quantitative understanding of the response of the chemical modification in iron-containing minerals to environmental changes.

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## Spin transition of Fe<sup>2+</sup> in ringwoodite (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> at high pressures

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Electronic spin transitions of iron in the Earth's mantle minerals are of great interest to deep-Earth researchers because their effects on the physical and chemical properties of mantle minerals can significantly affect our understanding of the properties of the deep planet. Polycrystalline samples were synthesized in a multi-anvil apparatus using <sup>57</sup>Fe-enriched starting material ((Mg,Fe)O-SiO<sub>2</sub> mixture) at conditions of approximately 22 GPa and 2000 K. Energy dispersive x-ray elemental mapping and electron diffracton study of the sample showed that Fe predominantly presents in the ringwoodite phase  $\gamma$ -(Mg<sub>0.75</sub>,Fe<sub>0.25</sub>)<sub>2</sub>SiO<sub>4</sub>.

The electronic spin states of iron in ringwoodite were studied at high pressures up to 82 GPa using synchrotron Mössbauer spectroscopy (NFS) in a diamond anvil cell (HPCAT, Sector 16, APS, ANL). At ambient conditions, the NFS spectra reveal two non-equivalent iron species (Fe<sup>2+</sup>)<sub>1</sub> and (Fe<sup>2+</sup>)<sub>2</sub> which can be attributed to octahedral and tetrahedral sites in the cubic spinel structure of ringwoodite, respectively. High-pressure NFS spectra showed the disappearance of the hyperfine quadrupole splitting of the Fe<sup>2+</sup> ions in both sites at approximately 45-70 GPa, indicating an electronic high-spin to low-spin transition. The spin transition exhibits a continuous crossover nature and is reversible at decompression.

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## Subseafloor basalts as fungal habitats

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The oceanic crust makes up the largest potential habitat for life on Earth, yet next to nothing is known about the abundance, diversity and ecology of its biosphere. Our understanding of the deep biosphere of subseafloor crust is, with a few exceptions, based on a fossil record. Surprisingly, a majority of the fossilized microorganisms have been interpreted or recently re-interpreted as remnants of fungi rather than prokaryotes [1-4]. Even though this might be due to a bias in fossilization the presence of fungi in these settings can not be neglected.

We have examined fossilized microorganisms in drilled basalt samples collected at the Emperor Seamounts in the Pacific Ocean. Synchrotron-radiation X-ray tomography microscopy (SRXTM) studies has revealed a complex morphology and internal structure that corresponds to characteristic fungal morphology. Chitin was detected in the fossilized hyphae, which is another strong argument in favour of a fungal interpretation. Chitin is absent in prokaryotes but a substantial constituent in fungal cell walls.

The fungal colonies consist of both hyphae and yeast-like growth states as well as resting structures and possible fruit bodies, thus, the fungi exist in vital colonies in subseafloor basalts. The fungi have also been involved in extensive weathering of secondary mineralisations. In terrestrial environments fungi are known as an important geobiological agent that promotes mineral weathering and decomposition of organic matter, and they occur in vital symbiosis with other microorganisms. It is probable to assume that fungi would play a similar role in subseafloor basalts and have great impact on the ecology and on biogeochemical cycles in such environments.

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## Simultaneous measurement of CCN activity and chemical composition of fine aerosols at Noto peninsula, Japan, in autumn 2012

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For the quantitative evaluations of cloud condensation nucleus (CCN) characteristics in the East Asia, CCN activity and chemical composition of atmospheric aerosols in submicrometer size range were measured at Noto Ground-based Research Observatory (NOTOGRO), located at the tip of Noto peninsula, facing the Sea of Japan, in autumn 2012.

In the atmospheric measurement, the CCN efficiency spectra, where CCN number fraction is plotted against the diameter of aerosols, were obtained at four different supersaturation (SS) conditions (0.1%, 0.2%, 0.5% and 0.8%). Hygroscopicity parameters  $\kappa$  [1], which depends on the chemical composition of aerosols, were estimated by the analysis of the CCN spectra. The bulk chemical composition of non-refractory submicrometer-sized aerosols was also measured by an aerosol chemical speciation monitor (ACSM).

The CCN activation diameters of ambient aerosols were clearly larger than those of pure ammonium sulfate under each SS condition. From the relationship between the estimated  $\kappa$  values and the CCN activation diameters, it was suggested that organics contributed to the aerosol mass especially in the size range of less than 100 nm. The contribution of organics observed in this study, based on the analysis of CCN spectra, was more apparent than those for other sites in East Asia [2, 3]. The bulk chemical composition derived by ACSM also indicated the significant mass fraction of organics in the submicrometer size range. The negative correlations between organic mass fraction and cloud droplets' diameters were observed especially under low SS conditions (<0.2%), suggesting that the initial growth rates of cloud droplets might slow by certain organics.

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## Clarification for Boron Sorption Mechanism in Coprecipitation with Magnesium Hydroxide

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Although boron is absolutely essential in various industries, especially in glass industry, the high contaminant levels of boron in water are regulated in several countries because of its toxicity. While ion-exchange resin is commonly used to remove boron from wastewater, it is relatively expensive. In this study, boron removal by coprecipitation method using magnesium salt has been investigated. The objective of this study is to clarify how coprecipitation of boron with magnesium hydroxide occurs in order to achieve cost efficient way to treat wastewater.

We carried out three kinds of experimental studies; (i) sorption isotherm formation, (ii) XRD analysis, (iii) NMR analysis. In general, when pH is below 9.2, the predominating species is orthoboric acid, which is less adsorptive because of its low electrical activity [1]. Therefore, we carried out the coprecipitation experiments at pH 10.5 and 0.3 of ion strength. Indeed, we could achieve the best adsorption efficiency of boron to magnesium hydroxide at pH 10.5.

We found that the sorption isotherm was BET type, which suggested that the sorption mechanism of boron adsorption was changed as the initial B/Mg molar ratio increased. From XRD analysis, the crystal structure of the precipitation corresponded with magnesium hydroxide when the initial B/Mg molar ratio was less than 0.4, whereas uncertain amorphous precipitation and carbonate hydromagnesite were formed when the initial B/Mg molar ratio was larger than 0.4. Formation of the uncertain amorphous precipitation indicated that surface precipitation was formed and related to boron uptake to magnesium hydroxide when the initial B/Mg molar ratio was larger than 0.4. NMR analysis showed that boron was adsorbed onto the surface of magnesium hydroxide as three-coordinate boron. These results suggested that a part of boron was precipitated or intercalated with uncertain amorphous precipitation as three-coordinate boron during coprecipitation with magnesium hydroxide.

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## Seeing through the haze: Testing the existence of a Neoproterozoic bistable organic-rich atmosphere

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The Great Oxidation Event (GOE; ~2.45–2.32 Ga) represents the onset of pervasive atmospheric oxygenation; however, ~2.7 Ga cyanobacterial microfossils and biomarkers [1] coupled with additional geochemical evidence [2], suggests a potentially earlier origin for photosynthetic O<sub>2</sub> accumulation. This temporal disparity implies either localised O<sub>2</sub> production or transient small rises ('whiffs') in atmospheric O<sub>2</sub> [2]. Despite the emerging data, large uncertainties surround the composition and the evolution of the Neoproterozoic atmosphere.

Analyses of sediments from the Campbellrand-Malmani platform (GKF01; ~2.65–2.5 Ga) suggest localised O<sub>2</sub> production, in a reducing atmosphere [3]. Importantly, within GKF01, large deviations in  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  correlate with pronounced <sup>13</sup>C-depletions in  $\delta^{13}\text{C}_{\text{Org}}$ , implying increased sedimentary incorporation of methanogenic carbon [3, 4]. Photochemical model simulations corroborate these data and predict the persistence of a bistable atmosphere poised between clear-skies and hazy conditions, implicating methane as an important component of the Neoproterozoic atmosphere.

Here, a new multiple S-isotope record from age-equivalent successions in W. Australia, combined with proxies for ocean redox and nutrient availability, will test the envisaged coupling between oceanic and atmospheric chemistry [3] whilst examining the drivers that link the two.

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