

## Strongly reduced gases emitted during flood magmatism and their environmental consequences

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We use thermodynamic calculations to show that high-temperature interaction between basaltic magma and organic matter can profoundly affect the redox state of the magma and of the gases in equilibrium with it. Our calculations simulate the incorporation into the gas-melt system of organic compounds like CH and CH<sub>2</sub> and take into account S-H-O-C gaseous species at temperatures and pressures in equilibrium with a basaltic liquid. We predict that the assimilation of less than 1 wt% organic matter produces gases with very unusual compositions that are CO-dominated and have H<sub>2</sub>O and CO<sub>2</sub> as minor constituents. The crystallization of graphite and native iron is also predicted as a consequence of CH or CH<sub>2</sub> incorporation.

We combine our calculations with existing petrological observations on the Siberian Traps to assess the relevance of this process for the emplacement of voluminous magmatic intrusions in the coaliferous sediments of the Tunguska Basin. Critical is the presence of magmatic graphite and native iron in igneous mafic rocks, which allows to constrain the minimum amount of organic matter assimilated and the composition of the produced gases. We also present an estimation of the fluxes of the exceptional CO-dominated gas emissions, which are likely to have been produced by the emplacement of the Siberian intrusions. We finally evaluate the fate of such gases during their diffusion in the atmosphere, by using a regional 3D atmospheric model coupled to a tropospheric chemistry one.

## The chemistry and the environmental impact of the Romanian phosphogypsum

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The aim of this paper is the mineralogical and geochemical description of phosphogypsum from a Romanian location for an accurate assessment of its environmental impact. Phosphogypsum is a technogenic (mineralurgic) by-product from the extraction of phosphoric acid from raw phosphate ore, consisting mainly of apatite [ideal formula: Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F, OH, Cl)]. The extraction technology uses normally the sulfuric acid to attack the apatite mineral. The phosphogypsum contains (in weight percentages) 32% CaO, SO<sub>3</sub> 45% and 15% water of crystallization, with approximately 8% of impurities.

The chemical composition of phosphogypsum is influenced by three factors: 1) by the type of phosphate rock (apatitic rock) used as primary material, and also by the nature and distribution of the trace elements of the rock; 2) by the processes of manufacturing of the phosphoric acid: the extraction process of the phosphogypsum, having as an intermediar product the calcium dehydrate, leads to the formation of some phosphogips, witch have a high level of contamination than their homologue, in some compounds as: Mn<sub>2</sub>O<sub>3</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>; 3) by the dumps age or stored phosphogypsum deposits, which, due to the percolation of the meteoric wather, have the tendency of lousing, through solubilisation, a part of some trace elements. Some of the chemical, mineralogical and radiometric characteristics of the phosphogypsum, but also its use as a primary material can directly influence its impact on the environment and also on the human health collectivises.

The main factors, that have a major impact on the environmental safety, but also on the phosphogypsum recycling, are the radioactivity, the toxic elements contents, pore water acidity, mineral's impurity, the contents in rare elements.

The pollutants emitted from the phosphogypsum dumps have a potential impact on the environment, affecting both the people and the animals. The potential pathways of human exposure to these pollutants include: the irradiation with gamma rays; the content in toxic elements; contaminated dust and other elements which can provoce the cancer; the ingestion of contaminated groundwater.

## Reliance of the rate of dissolution of the SON68 glass on $\text{SiO}_2(\text{aq})$ : New quantification using interferometry

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At present, one of the most vexing problems confronting experimentalists and modelers alike is how nuclear waste glasses will react long-term in the repository environment. Many of the experiments that underpin modeling efforts have been conducted at conditions that are not germane to answering these questions. One of the most important constituents in natural subsurface waters is dissolved silica [ $\text{SiO}_2(\text{aq})$ ], and efforts are underway to understand the dependence of the dissolution rate on this component. A method to determine rates accurately in solutions containing high concentrations of  $\text{SiO}_2(\text{aq})$  is needed.

We present evidence that rates of glass dissolution can be quantified by using a Vertical Scanning Interferometer (VSI) over a range of  $\text{SiO}_2(\text{aq})$  concentrations. Polished glass monoliths (SON68) were exposed to solutions containing 0 to  $5.46 \times 10^{-3}$  mol/L  $\text{SiO}_2(\text{aq})$  at 90°C and pH = 9. Both batch (static) and flow-through reactor systems were employed. In the former, the surface area of glass to volume of solution ratio (SA/V) was kept at a low value, ensuring that the system maintained a constant chemical affinity. In the flow-through systems, the SA/V ratio was higher and the release of elements into solution was monitored to ensure steady-state values. Dissolution rates by VSI were determined by comparing the height of the reacted surface to that of a pristine reference surface, and these rates were compared against those determined by assaying the effluent solutions from the flow-through experiments. The results revealed a close correspondence between the two methods for determining rates, and both methods indicated a linear dependence of the rates upon the concentration of  $\text{SiO}_2(\text{aq})$  in solution [ $\log R = -1.37 \times 10^{-2}(\text{Si}) - 5.41$ ]. This linear dependence shows that the rate can be quantified at conditions pertinent to the disposal environment and that a mechanistic basis for predicting rates can be realized.

## Smoke aerosol emission source analysis from satellite and airborne measurements

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Accurate estimation of smoke emission source strength from active fires is essential for modeling smoke emission fluxes, transport, atmospheric interactions, and impacts on air quality and climate. For several decades, researchers have made efforts to estimate smoke emissions from ground-based measurements, but the spatial and temporal coverage is severely limited. The rapid growth of satellite measurement capability during the last decade has provided the potential to overcome these limitations by covering the entire globe for long periods of time. However, satellite remote-sensing methods are faced with new challenges as they attempt to use instantaneous observational snapshots to address continuous and highly variable processes such as fires and their emissions. The result is that, although the satellite enables more ground to be covered, uncertainties in quantifying emissions still remain, and may be even greater, compared to the ground-based methods. One of the promising ways to address this issue is the use of airborne measurements to bridge the spatial and temporal scales between the regional-scale satellite snapshots and landscape-scale, longer-duration processes of fire behavior and emissions. The ARCTAS summer campaign that was conducted in Canada in June–July 2008 provides a unique opportunity to demonstrate this approach with regard to closely exploring improved understanding of smoke emission mechanisms by remote sensing. In this talk, we will show preliminary results of using the vertical scans of plumes from the Cloud Absorption Radiometer (CAR) instrument aboard the NASA P-3 aircraft to complement the analysis of fire radiative power (FRP) and aerosol optical depth (AOD) measurements from MODIS aboard the Terra and Aqua satellites, and near-source plume-height measurements from MISR aboard Terra, to better understand the relationships between them, and elaborate the emission rates, spatial characteristics, and injection processes of smoke particulate matter.

## Characteristics of the Ruwai base metal-Ag skarn in Tertiary middle Kalimantan volcanic arc, Indonesia

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This study is dealing with geology and characteristics of mineralogy, geochemistry and physicochemical conditions of hydrothermal fluid responsible for the formation of the Ruwai skarn base metal (Pb-Zn-Cu)-Ag deposit in Tertiary middle Kalimantan volcanic arc, Indonesia. The formation of Ruwai skarn is genetically associated with calcareous rocks consisting of limestone and siltstone (derived from marl?) and controlled by NNE-SSW-trending strike slip faults and localized along N 70° E-trending thrust fault, which also acts as contact zone between sedimentary and volcanic rocks in the area. The Ruwai skarn is mineralogically characterized by prograde alteration (garnet and clino-pyroxene) and retrograde alteration (epidote, chlorite, calcite and sericite). Garnet is of andraditic composition, whereas clino-pyroxene is identified as wollastonite, diopside and hedenbergite. Both garnet and clinopyroxene show a petrographic and chemical zonation. Ore mineralization is typified by sphalerite, Ag-rich galena and chalcopyrite, which formed at the early retrograde stage. Galena is typically enriched in silver up to 0.45 wt% and bismuth of about 1 wt%. Geochemically, SiO<sub>2</sub> is enriched and CaO is depleted in limestone, consistent with silicic alteration (quartz and calc-silicate) and decarbonatization of the wallrock. The measured resources of the deposit are 2,297,185 tonnes at average grades of 14.98 % Zn, 6.44 % Pb, 2.49 % Cu and 370.87 g/t Ag. Ruwai skarn orebody originated at moderate temperature of 250-266 °C and low salinity of 0.3-0.5 wt.% NaCl eq. The late retrograde stage formed at low temperature of 190-220 °C and low salinity of ~0.35 wt.% NaCl eq., which was influenced by meteoric water incursion at the late stage of the Ruwai base metal-Ag skarn formation. Further exploration of the skarn extension in the prospect area should consider the structural setting, lithologic distribution and the presence of the diagnostic calc-silicate minerals.

## Pressure-induced phase transitions and H-D isotope effects in portlandite

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Ca(OH)<sub>2</sub>, portlandite, has a CdI<sub>2</sub> type structure and is one of the simple hydrous minerals. A crystal-to-crystal phase transition occurs around 10 GPa at room temperature in various pressure transmitting media [1, 2]. In brucite, which has an iso-structure of portlandite, H-D isotope effect on the compressibility was found from neutron diffraction [3]. In our study, the isotope effect on the pressure-induced responses was studied in order to clarify the phase transition mechanism accompanied by the geometrical change of hydrogen bonding for neutron diffraction studies in future.

Powder samples were synthesized by hydration of CaO powders with water (or D<sub>2</sub>O) in a Teflon lined stainless steel autoclave at 240°C for one week. The single-crystals were obtained by recrystallizing from powder. These samples were loaded in clamped DACs with a few small ruby chips. As a pressure medium, 4:1 methanol-ethanol mixture or He gas was used. IR absorption spectra were measured at the IR synchrotron radiation beamline BL43IR at SPring-8. Angular-dispersive synchrotron X-ray diffraction experiments up to 25 GPa were performed on the BL-18C beamline in the Photon Factory (PF), KEK.

No remarkable difference between Ca(OH)<sub>2</sub> and Ca(OD)<sub>2</sub> samples was found in the compression behaviors from powder XRD patterns. They were consistent with the previous studies [4-7]. The OH(OD) vibration peaks of IR spectra were split at 6-7 GPa for single-crystals in He medium. No significant difference suggesting the isotope effect was found in the phase transition pressure. The hydrostaticity was found to contribute strongly to the process of the phase transition or amorphization. This implies that neutron diffraction of portlandite needs to be carefully measured under controlled stress conditions using large-volume presses.

[1] Catalli *et al.* (2008) *GRL* **35**, L05312. [2] Ekbundit *et al.* (1996) *J. Solid State Chem.* **126**, 300-307. [3] Horita *et al.* (2010) *PCM* **37**, 741-749. [4] Meade & Jeanloz (1990) *GRL* **17**, 1157-1160. [5] Nagai *et al.* (2000) *PCM* **27**, 462-466. [6] Pavese *et al.* (1997) *PCM* **24**, 85-89. [7] Xu *et al.* (2007) *J. Solid State Chem.* **180**, 1519-1525.

## Evolution of the African continental crust from Pb-Hf-O isotope systematics of detrital zircons

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To better understand the evolutionary history of the African continental crust, we have determined U-Pb ages, Lu-Hf and O isotopic compositions of ca. 450 detrital zircons from the Congo, Nile, Orange, Zambezi and Niger Rivers. The U-Pb isotopic data reveal the lack of >3.2 Ga zircons in the river sands, and distinct peaks at 2.7-2.5, 2.1-1.9, 1.2-1.0 and 0.9-0.6 Ga. The  $\epsilon\text{Hf}(t)$  population shows that many zircons, even those having Archean U-Pb ages, crystallized from magmas involving an older crustal component (Figure 1). The O isotopic analyses reveal that ca. 70% of the zircons have  $\delta^{18}\text{O}$  values higher than 6.5 (Figure 1), indicating that reworking of supracrustal material is important in the granitoid crust formation. However, no >2.0 Ga detrital zircons have  $\delta^{18}\text{O}$  values higher than 8.0, suggesting restricted contribution of mature sediment to granitoid magma genesis in the Archean and early Proterozoic. We calculated Hf isotopic model ages for the zircons to estimate the mean mantle-extraction ages of their source materials. The oldest zircon Hf model ages of ca. 3.4 Ga suggest that some crust generation had taken place by that time, and that it was subsequently reworked into <3.2 Ga granitoid crust. The Hf model age distribution of the zircons having  $\delta^{18}\text{O}$  values lower than 6.5 shows a prominent peak at 1.1-0.8 Ga, implying rapid generation of the continental crust at that time.

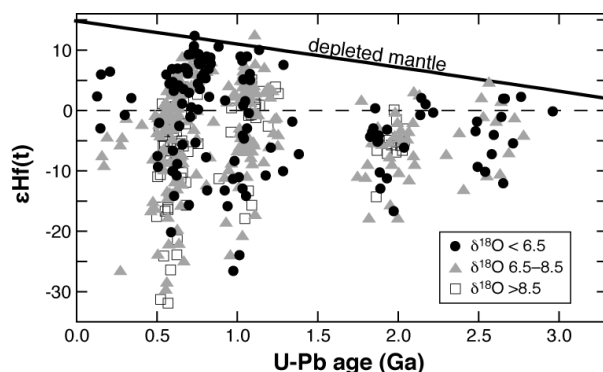


Figure 1: Plot of age vs.  $\epsilon\text{Hf}(t)$  for African detrital zircons.

## Biogeochemical processes in mud-volcano sediments from the Kumano forearc basin, Japan

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Remarkable populations of microbial life have been observed in global subseafloor environments. However, it remains largely unknown if the deep-derived diapiric structure provides potential habitats for subseafloor life or not. Here, we investigated microbial communities and biogeochemical processes in mud-volcano subsurface sediments down to 20 meters from the summit, obtained from the Kumano forearc basin in the Nankai Trough during the CK09-01 D/V *Chikyū* training cruise in 2009.

Pore water extracted from the cored sediments showed significantly low chlorinity to seawater (averaged in 23% of that in seawater), indicating that dehydrate reaction of clay minerals had previously occurred in the deeply buried sedimentary layer. The cored sediments contained relatively low population of microbial cells ( $<10^4$  cells/cm<sup>3</sup>). The  $\delta^{13}\text{C}$  value of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) increased with the coring depth, reaching +40‰ at 3 meters below the seafloor (mbsf). The highly <sup>13</sup>C-enriched values are possibly due to strong microbial reduction of DIC to <sup>12</sup>C-enriched products. The hydrogen isotopic composition of methane ( $-181\pm 2\%$ ) and magnitude of the carbon isotopic fractionation between DIC and methane ( $75.6\pm 2.8\%$ ) below 3 mbsf suggest the significant contribution of hydrogenotrophic methanogenesis as the source of methane. The  $\delta^{13}\text{C}$  value of acetate was appeared to increase with the sediment depth (from -41 to -22‰), synchronous to the increase of  $\delta^{13}\text{C}_{\text{DIC}}$ . The significant isotopic fractionation between DIC and acetate ( $54.0\pm 6.9\%$ ) indicates that the principal process producing acetate is homo-acetogenesis via the reductive acetyl-CoA pathway. Radioactive tracer experiments exhibited relatively high activities of homo-acetogenesis (14–34,900 pmol/cm<sup>3</sup>/day) and hydrogenotrophic methanogenesis (0.6–128 pmol/cm<sup>3</sup>/day), consistently suggesting that autotrophy plays significant biogeochemical roles in the mud-volcano subseafloor microbial ecosystem.

## Enhanced chemical weathering during early Triassic in response to the collapse of terrestrial ecosystem after the end-Permian mass extinction

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The vegetation recovery after the end-Permian mass extinction was delayed by > 5 m.y. until middle Triassic. It is demonstrated that the collapse of terrestrial vegetation enhanced physical weathering during early-middle Triassic, whereas its impact on chemical weathering intensity has not been investigated. Here, we investigate the variations of chemical weathering intensity and biogenic Si flux from lower to middle Triassic pelagic siliceous sequence of the equatorial Panthalassa in Japan, whose cyclostratigraphy is well established [1, 2]. Our results suggested that the chemical weathering intensity and the biogenic Si flux during early Triassic were extremely high relative to middle Triassic and decreased during middle Triassic. Also, the calculated biogenic Si budget on pelagic Panthalassa during early and middle Triassic was several times larger than total Si budget of global ocean today [3], suggesting that pelagic siliceous sequence at equatorial Panthalassa was the major sink of oceanic Si. Hence, the changes in biogenic Si flux on pelagic Panthalassa could reflect changes in global chemical weathering intensity in time scales larger than the residence time of Si in the ocean (> 10 kyr [3]). Therefore, the increase and following decrease in chemical weathering intensity during early to middle Triassic would have been related to the collapse of terrestrial vegetation and its recovery during early Triassic.

[1] Ikeda *et al.*, (2010), *Earth Planet. Sci. Lett.*, **297**, 369-378.

[2] Sakuma *et al.*, in review *Island Arc* [3] DeMaster *et al.*, (2002), *Deep-Sea Research*, **49**, 3155-3167

## Trace metal concentrations and Pb isotopes of sediments from Barkley Sound, British Columbia

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Port Alberni is home to several industries (e.g., pulp and paper mills), responsible for releasing significant amounts of heavy metals (e.g., As, Cd, Pb and Hg) into Alberni Inlet every year [1]. Alberni Inlet may carry this metal effluent into Barkley Sound, located on the west coast of Vancouver Island, British Columbia (BC), home to economically important oyster farms. Alberni Inlet supplies freshwater to Barkley Sound and the headwaters are proximal to Port Alberni. Emissions associated with recreational boating in Barkley Sound and traffic in the lower mainland and on Vancouver Island are other potential sources of Pb pollution. We determined As, Cd and Pb metal concentrations and Pb isotopic compositions in sediment samples from Barkley Sound, collected from transects along Imperial Eagle Channel, Trevor Channel, and from Junction Passage, to assess metal contamination associated with local industries and trace the source of Pb pollution.

Metal concentrations for sediments from Barkley Sound range from 6.20 to 10.8 ppm for As, from 0.36 to 0.56 ppm for Cd, and from 4.91 to 17.5 ppm for Pb. The highest concentrations of As and Cd were observed in sediments from Junction Passage, directly downstream from Alberni outlet. In general, a decrease in Pb, As and Cd in the sediment was observed along NW-SE transects, i.e. towards the open ocean. Sediment  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios increase with increasing distance from Port Alberni, suggesting increasing natural contributions. The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios (1.1783 to 1.1909) were primarily within the high end of the range reported for BC road dust [2], with the exception of that of sediment from the most distal site in Trevor Channel, with an isotopic composition closer to that of North Pacific sediments [3]. Our study shows that metal concentrations in Barkley Sound sediments are controlled in large part by anthropogenic activities and industrial inputs to Alberni Inlet.

[1] Environment Canada (2009) National Pollutant Release Inventory Facility (NPRI) [2] Preciado *et al.* (2007) *Water Air Soil Poll* **184**, 127-139. [3] Carpent *et al.* (2010) *Gold. Conf. Absr.* 144

## High fluctuations of suspended load in a tidal influenced river mouth, west coast of India

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Suspended load of water bodies play a major role in studies related to pollution levels, turbidity, source and sink of sediments, sediment transport, etc. Proper sampling method brings out acceptable interpretations. Many times, one time observation of suspended sediment load is considered as representative of that aqueous ecosystem. However, one time observation of suspended sediment load may be less objectionable in substantiating the interpretation of the observation when aqueous body is a land locked lake or undisturbed fresh water river system. Therefore, the present study was carried out to check the validity of one time sampling. The study involved, every 2 hours observation of suspended sediment load at surface, mid depth and at near bottom of a tidally influenced river mouth (River Dahej), at west coast of India, for 2 days. The obtained data reveal high fluctuations in the volume of suspended sediment matter. Various parameters such as flood tide, ebb tide, slack period, spring tide, neap tide, fresh water-sea water mixing, water currents, etc., must be controlling the suspended sediment matter concentration in an environment which is influenced both by marine and riverine ecosystem. This study therefore, reveals the necessity of an acceptable sampling protocol considering all the controlling parameters so that interpretations of the observations are truly representative of the conditions of the involved aqueous ecosystem.

## Effect of lake sediment application on soil structure assessed by means of X-ray computed microtomography

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It is known that lake sediments applied to agricultural soils may improve soil fertility on dry sandy soils by increasing soil carbon storage and water holding capacity. In contrast, the effect of lake sediments on soil structure has not been well documented yet even though some of the documented effects must be linked to soil morphology. X-ray computed microtomography enables to characterize objects down to 50  $\mu\text{m}$  or less and has recently successfully been applied to soil. The aim of this study was therefore to analyze, by means of X-ray computed microtomography, the structure of soil amended with lake sediments compared to a control.

At the long-term experimental site Lietzen in Brandenburg, lake sediments were applied to the soil after harvest at rates of 15 and 70 t/ha. At two locations within the 70 ha sized field, two undisturbed soil samples each (diameter 3.1 cm, height 4 cm) were taken from 0-4 cm soil depth. They were analysed with a 320 kV micro focus X-ray tube (spatial resolution 1/1000 of maximum sample diameter). The morphometric analysis included the determination of the overall pore volume and the local variance in the samples.

The morphological analysis showed that differences between amended and control soil were minor. In contrast, soil texture which differed strongly between the two sampling sites seemed to profoundly affect soil microstructure (pore volume, soil heterogeneity). It is assumed that the observed differences in soil structure are ultimately linked to soil texture-induced differences in soil biological activity.

The results show that more research is needed to entangle the effects of soil texture vs. management effects on soil microstructure and to identify mechanistical links between soil structure and soil biota under field conditions.

## The Lomagundi-Jatuli $\delta^{13}\text{C}$ -Event revisited

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The Lomagundi-Jatuli Event (LJE) is characterized by a positive carbonate carbon isotope ( $\delta^{13}\text{C}_{\text{carb}}$ ) excursion [1, 2] in the aftermath of the Great Oxidation Event (GOE). Results reported from different successions, ranging in age from 2.4 to 2.2 Ga, imply that the LJE is global in nature [3, 4, 5, 6]. Assuming that the atmospheric/ oceanic dissolved inorganic carbon pool is faithfully archived in respective carbonate rocks, this carbon isotope excursion would indicate a shift in  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  of at least  $\sim 5\text{‰}$  for the duration of the LJE. The most likely explanation for this strong shift in  $\delta^{13}\text{C}_{\text{carb}}$  is an enhanced biological  $\text{CO}_2$ -fixation and organic carbon burial leaving the residual pool enriched in  $^{13}\text{C}$ . However, an alternative view has recently been proposed [7].

Here, we report paired analysis of  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  for rocks capturing the LJE. These were obtained by the Fennoscandian Arctic Russia-Drilling Early Earth Project (FAR-DEEP). Carbonates show the typical positive  $\delta^{13}\text{C}_{\text{carb}}$  values. In contrast, however, the organic matter does not record a corresponding positive shift in  $\delta^{13}\text{C}_{\text{org}}$ . Standard isotope mass balance provides no satisfactory explanation. Hence, alternative explanations are in need!

[1]Schidlowski *et al.* (1975), *GCA* **40**, 449-455. [2] Melezhnik *et al.* (1999), *Earth Sci. Rev.* **48**, 71-120. [3] Baker & Fallick (1989) *Nature* **337**, 352-354. [4] Karhu & Holland (1996), *Geology* **24**, 867-870. [5] Maheshwari *et al.* (2010), *Precamb. Res.* **182**, 274-299. [6] Tang *et al.* (2011), *Gondwana Res.* **19**, 471-481. [7] Hayes & Waldbauer (2006) *Phil. Trans. Roy. Soc. B* **361**, 931-950.

## Coupled geochemical and foraminiferal response to environmental changes during the deposition of Upper Cretaceous oil shale in the Negev, Israel

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The accumulation of a 40 m thick oil shale sequence during the latest Campanian marks a major change in the dynamics of the Late Cretaceous southern Tethys upwelling system. Based on the vertical distribution of foraminiferal taxa, Ashckenazi-Polivoda *et al.* [1] established a high resolution paleoenvironmental scheme, defining five planktic (P-Type) and five benthic foraminifera (B-Type) assemblages which thrived under distinct bottom-water aeration and surface water productivity conditions.

Principal component analysis of major and trace elements concentrations in the studied sequence allows distinguishing three factors. The first reflects the interplay between biogenic-carbonate (Ca, Sr) and terrigenous input (Al, Si, K, Ti, V, Fe, Ga, Nb, Ba, Pb, Th). The second mirrors the degree of bottom water oxygenation ( $\text{C}_{\text{org}}$ , S, Ni, Cu, Zn, As, Cd, Mo, U vs. Mn), while the third factor stands for conditions that promoted phosphorite deposition (P, Y, La, U). The comparison of these chemostratigraphic features with the distribution of the foraminiferal assemblage types as defined in [1] points to a strong interdependence between these geochemical and micropaleontological environmental indicators. The distribution of the planktic assemblages P-Types 1 and 4, and the benthic assemblage B-Type 4 parallels the variations in the degree of bottom water oxygenation and detrital input. P-Type 1 and 2 (high *Heterohelix*) assemblages coincide with a gradual decrease in biogenic carbonate production and a relative weak anoxic response to the increase in terrigenous input. In contrast, assemblages P-Type 4 (dominance of *Globigerinelloides*) and B-Type 4 (triseriate buliminids and *Gavelinella*), limited to the base of the oil shale, are characterized by strong anoxia and high carbonate production, as reflected by scores of factors 1 and 2.

[1] Ashckenazi-Polivoda *et al.* (in press) *Palaeogeogr. Palaeoclimatol. Palaeoecol.* DOI10.1016/j.palaeo.2011.02.018

## Mobility and bioavailability of some potentially harmful elements around an industrial contaminated environment (Estarreja, Portugal)

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Located in north central Portugal the industrial Chemical Complex of Estarreja (CQE) is composed of several chemical industries that could cause environment pollution. The most important inputs into the environment are chiefly related to past industrial activities, with the production of sulphuric acid from arsenopyrite roasting (e.g. As, Cu, Ni, Pb and Zn) and from a chloralkali plant (e.g. Hg).

The main purpose of this study was to evaluate the levels of some heavy metals and arsenic in soils and forage plants from Estarreja and from a reference site (Ouça, with no significant industry but a similar geology, pedology). These soils are sandy soils, often used as pasture and agricultural land. In Estarreja 90 topsoils and 27 forage plants were collected; in Ouça 20% of these numbers were sampled. Both soils and plants (separated into roots and green shoots) were analyzed in the same way, extraction with aqua regia and analysis by ICP/ES & MS, for 32 chemical elements. Three single extractants (water; ammonium acetate; EDTA) were used to assess the mobile and plant available fraction of some potentially harmful elements.

The first results show high levels of As and Hg in Estarreja compared to those given in the international guidelines. The maximum concentrations found in the soils are above 10.000 mgkg<sup>-1</sup> for As and above 100 mgkg<sup>-1</sup> for Hg. In green shoots, the maximum concentrations found are 255 mgkg<sup>-1</sup> for As and 5 mgkg<sup>-1</sup> for Hg. The spatial distribution of these elements shows a typical anthropogenic pattern, with the highest values near the factories and sewage outlets. It was possible to identify an area around the factories and sewage outlets where the median concentrations for As and Hg are more than 10 times higher than the median concentrations found in the reference area, which are close to the national backgrounds [1]. The EDTA was the most effective extractant for all the elements, except Zn, which was higher in the ammonium acetate extracts. However, the amounts extracted with these three extractants are low (less than 5%) for As, Hg, Pb, Cu and Zn, thus attenuating the impact of high metal contents in soils of green areas often used as pasture land and agriculture.

[1] Inácio *et al.* (2008). *Journal of Geochemical Exploration*; 98: 22-33.

## Sequestering of phosphorus during freshening of a silled marine basin; Role of manganese

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We have documented sediment sequestering of phosphorus in the Bothnian Bay, northern Baltic Sea, during the last 7000 years, using a paleomagnetic dating method. High resolution sampling and multi-element analyses coupled with "absolute dating" of the sediment provides a powerful environmental record that can be used to foresee biogeochemical changes caused by climate-induced freshening of the Baltic and other silled marginal marine basins. Late Holocene freshening is pronounced in the Bothnian Bay, with a decline of surface salinity from 10-11‰ down to present day values between 1‰-3‰, consistent with the absence of a permanent halocline, and phosphorous limitation of primary production.

The P/Fe ratio in a 6-m-long piston core show distinct peaks above the time level 2500 years BP, closely related to temporal peak values for manganese, the Mn/Fe ratio and a major changes in magnetic susceptibility. We suggest that the changes in phosphorus sequestering in the core can be explained by the position of the suboxic zone at the time of deposition. A suboxic redox potential can be maintained in these layers if there is an excess of manganese that can oxidise formed sulphide in the sediment during burial. Particulate manganese maintains the suboxic redox level preventing dissolution of Fe-oxyhydroxides with associated phosphorus, at depth in the sediment. Today, the barrier between the sulfide zone and the sulfate zone is situated 0.5 m below the sediment surface. Trace metal data suggest that this zone has been located within the sediment during the whole lifetime of the core. Hence, a layer with high concentrations of Mn and Fe-oxyhydroxides, formed above the sulfide boundary, may pass through the sulfide barrier, leaving Fe-Mn oxyhydroxides in relative equilibrium below the active sulfide boundary.



## Water content of lithospheres deduced from xenoliths: The example of Kerguelen Islands and South African craton

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The formation of the Kerguelen crust since 110 Ma, through magma underplating, may represent a good analogue for continental growth in oceanic environment like it was during the Archean period. The study of water content of granulite xenoliths representative of Kerguelen deep crust and related mantle xenoliths offers the opportunity to: 1) evaluate the distribution of water along the Kerguelen lithosphere; 2) compare it to the content of the older lithosphere like for instance the South African cratonic lithosphere.

We measured water content from 10 granulite xenoliths and 5 mantle xenoliths from alkali basaltic lavas erupted on Kerguelen Islands on the Northern part of the Kerguelen plateau. The xenoliths are composed of two-pyroxenes granulites with spinel or garnet [1]. The analysis of water dissolved as H-related point defects in the main anhydrous phases was done by micro-FTIR with a spot size of 50 microns, a spectral resolution of 4 cm<sup>-1</sup> and with unpolarized beam following the procedure proposed by Kovacs *et al.* [2]. The water contents of pyroxenes from the granulite xenoliths (up to 180 and 330 ppm H<sub>2</sub>O for orthopyroxenes and clinopyroxenes respectively) are significantly higher than those from the mantle xenoliths.

The Kerguelen xenoliths are less hydrous than the ones from the Kaapvaal Craton [3] suggesting that the mantle source at the origin of their formation is less hydrous than the ones at the origin of the older deep crust formed beneath South Africa or the North Chinese cratons [4].

[1] Gregoire *et al.* (2001) *Contrib Mineral Petrol* **142**, 244-259. [2] Kovacs *et al.* (2008) *i93*, 765-778. [3] Ingrin *et al.* (2010) *EGU*. [4] Yang *et al.* (2008) *JGR* doi:10.1029/2007JB005541.

## Studies on annual variation of <sup>14</sup>C/<sup>12</sup>C ratios in plant samples by AMS

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Carbon-14 (T<sub>1/2</sub>; 5730yr) is one of the most important radionuclides produced by the reaction of cosmic ray with nitrogen in the upper atmosphere. Therefore, <sup>14</sup>C/<sup>12</sup>C ratios in plant materials should provide information on the past atmospheric <sup>14</sup>C levels which might be related to the variation of solar activities. The <sup>14</sup>C levels in the atmosphere are also affected by the anthropogenic sources such as nuclear weapons testing and accident of nuclear facilities. In this study, we have determined <sup>14</sup>C/<sup>12</sup>C ratios by AMS in three different plant materials, i.e. tree rings of Japanese Yaku-ceder, Japanese rice grains and tree rings of pine from Chernobyl area, for assessing the variation of atmospheric <sup>14</sup>C.

In order to know the natural variation of <sup>14</sup>C, we used tree rings of old Yaku-ceder (1139 year-old) and focused on a period between 1000-1100 A.D. As a result, we found a peak around 1050 A.D. This suggests that the solar activity was weak in this period.

Results obtained for rice grain samples (1950-2009 A.D.) showed that there was the highest peak around 1963 due to nuclear weapons testing and the values decreased gradually. Residence time of the produced <sup>14</sup>C was calculated to be about 11 years.

Tree rings of pine collected from the vicinity of Chernobyl NPP was used to assess the release of <sup>14</sup>C at the accident, which occurred in late April 1986. A peak of <sup>14</sup>C/<sup>12</sup>C ratio clearly observed in the tree ring of 1986. However, the ratio varied widely within the tree ring. This heterogeneous distribution should be due to the short time releases (about 10 days) of <sup>14</sup>C during the accident. To examine this, we have separated early and late wood and found that the early wood contained markedly high <sup>14</sup>C and the late wood contained low <sup>14</sup>C compared to whole ring of the same year.

## Effects of thermal and salinity stresses on growth of aposymbiotic and symbiotic primary polyps

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In order to better understand the effects of high thermal and low salinity stresses on coral calcification from the aspect of coral-algal symbiosis, aposymbiotic (lacking symbionts) and symbiotic coral primary polyps were experimentally exposed to several seawater temperatures (27 ~ 33°C) and salinities (26 ~ 34 treatments). Calcification rates of polyp skeletons with zooxanthellate (symbiotic) were higher than those without zooxanthellate (aposymbiotic) in both the experiments even under high thermal and low salinity stresses.

Symbiotic polyps showed non-linear calcification responses to thermal stresses whereas aposymbiotic demonstrated linear increase of calcification responses according to the increase of temperature. Both aposymbiotic and symbiotic polyps showed the linear decreases of calcification rates according to the decrease of salinity. Our results suggest that future global warming may have negative impact on coral calcification at the primary polyp processing symbionts. In addition, low salinity stress, which would be caused by increase of the intensity of local floods related to future climate change, would certainly decrease coral calcification.

## Peridotite xenolith inferences on the formation and evolution of the central Siberian cratonic mantle

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Ongoing multi-disciplinary studies of large and fresh (LOI ≤1%) mantle xenoliths from the Udachnaya kimberlite in the central Siberian craton address the structure, composition and origin of cratonic lithospheric mantle. Petrographic data document successive deformation of coarse garnet peridotites (with strong crystal preferred orientation) to form: (1) olivine grains that are broken but not recrystallised, (2) porphyroclastic, (3) fluidal mosaic microstructures [1]. Extremely high sub-Moho velocities recorded in some seismic profiles in the craton may reflect strong anisotropy of foliated coarse peridotites [2]. Both sheared and coarse peridotites occur near the base of the lithosphere (≥1300°C, ~6.8 GPa). Oxygen fugacity decreases with depth. The major element composition of the majority of refractory peridotites is consistent with melt extraction at 1-5 GPa; Mg# is ≤0.929. These rocks are depleted in Pd, less commonly in Pt, relative to Os-Ir-Ru. Re-Os ages ( $T_{RD}$ ) of the melt extraction residues range from 1.5 to 2.3 Ga (av. 1.8 Ga). 15-20% of coarse peridotites are enriched in opx and may have experienced silica addition in subduction settings.

The Proterozoic Re-Os  $T_{RD}$  ages of melt extraction residues from this and earlier [3] work indicate that most of the lithospheric mantle formed simultaneously with the assembly of the craton 1.8-2.1 Ga ago and is not coeval with the oldest exposed crustal rocks (2.6-3.5 Ga) [4]. More ancient mantle materials appear to come from volumetrically small terrains. The Siberian craton, and possibly other long-lived, thick, cold, diamond-bearing lithospheric domains, may have been created in the Paleoproterozoic rather than in the Archean.

[1] Ionov *et al.* (2010) *J. Petrol* **51**, 2177-2210. [2] Bascou *et al.* (2011) *EPSL* **304**, 71-84. [3] Pearson *et al.* (1995) *GCA* **59**, 959-977 [4] Rosen (2002) *Russ. J. Earth Sci.* **59**, 103-119.

## Stacked SIMS Spectra: Unravelling ion production in geological materials

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Ion microprobe analyses rely on the production of secondary ions from solid target materials. In the material science community, complexity in ion production is noted for even simple targets comprised of only a few elements. In geological materials, complex mass spectra result from the large number of elements present and their propensity to form molecular ions. The analyses of molecular species is a cornerstone of zircon age determinations but resolution of unwanted interferences is also required.

We have developed a protocol to measure SIMS spectra under varying analytical conditions (mass resolution, energy filtering). These spectra can be stacked to allow identification of relevant species and custom built software allows individual peaks to be scrutinised. A reference lookup list means that isobars can be readily identified.

The spectra have been obtained on SHRIMP-RG, an instrument that allows mass resolution up to 20,000. A combined faraday – ion counter detection system is rapidly switched depending on count rates. Energy filtering can be changed to establish the nature of the molecular interferences based on the progressive exclusion of polyatomic interferences with energy offset.

Thus far we have applied this technique to NIST glasses as well as minerals used for geochronology – zircon, monazite, and xenotime. For monazite, unresolved interferences in the Pb spectrum could potentially affect some analyses.

Having spectra from different matrices will also allow examination of ion production and speciation models, which will lead to a better understanding of zircon geochronology by SHRIMP.

## Trans-lithospheric variations in highly siderophile elements beneath the Ontong Java Plateau

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We determined highly siderophile element (HSE) concentrations and sulfur contents for 70 peridotite xenoliths from Malaita, Solomon Islands, which represent virtually the entire thickness (~120 km) of oceanic lithosphere beneath the Ontong Java Plateau. The major aim is to assess whether the fertile part of the suboceanic mantle yields suprachondritic Ru/Ir and Pd/Ir ratios and hence investigate the extent of non-chondritic HSE systematics in the Earth's mantle. To date, most constraints on PUM HSE characteristics come from subcontinental mantle due to the rarity of fertile samples from ophiolites and abyssal peridotites. In contrast, our Malaita sample set includes MORB source-like spinel lherzolites representing shallow lithosphere (<85 km) and garnet lherzolites from basal lithosphere (95-120 km), likely representing a deep-plume source [1]. A further aim is to examine the formation of an intralithospheric harzburgite layer (85-95 km). A previous Re-Os study revealed that the varying degree of Os-depletion uniquely recorded in this melt-depleted layer is intimately related to the ~122 Ma plateau magma production [2].

The new HSE data demonstrate that lherzolite and harzburgite, the two principal lithologies, display contrasting HSE patterns. Regardless of *P-T*, mineralogy and alteration indices, almost all lherzolites show coherent patterns with suprachondritic Ru/Ir and Pd/Ir, but chondritic Os/Ir and Pt/Ir. This supports the widespread occurrence of PUM-like compositions in Earth's mantle. In contrast, harzburgites display HSE depletion with decreasing sulfur content, coupled with highly fractionated patterns relative to PUM and systematically decreasing HSE/Ru, most likely resulting from progressive extraction of HSE residing in sulfide. We establish an order of HSE compatibility that may place key constraints on the mechanism and condition of formation of harzburgites and their extracted magma.

[1] Ishikawa *et al.* (2004) *J. Petrol.* **45**, 2011-2044. [2] Ishikawa *et al.* (2011) *EPSL* **301**, 159-170.

## Possible high-PGE-Au silicate melt/aqueous fluid in mantle wedge: Inferred from Ni metasomatism in Avacha peridotite xenolith

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Platinum-group elements (PGE) and gold (Au) have highly siderophile features and favor to be partitioned into metals and sulfides (such as the Earth's core). Among them, IPGE (Os, Ir and Ru) are well partitioned into residues relative to PPGE (Rh, Pt and Pd) and Au during partial melting of mantle peridotite, although PGE are not mobile during low-temperature alteration processes. We found Ni-rich domains in a highly metasomatized mantle peridotite xenolith (#159) from Avacha volcano, the Kamchatka arc, composed of ordinary mantle minerals (olivine, orthopyroxene, clinopyroxene, chromian spinel, and monosulfide solid solutions; MSS) with high-Ni contents, around aggregates of clays rich in Fe, Ni and S [1]. The high-Ni, -Fe, -S clays at the center of the Ni-rich domain show varied colors under the microscope, from yellowish to brownish. Most of them fill interstices or cracks, but some are observed as globular inclusions in olivine (Fo<sub>93</sub>). The MSS in this sample #159 rarely have quite thin hydroxide alteration rims. The Ni/(Fe + Ni) atomic ratio of the clays are varied (0-0.7) and show a good correlation with their color; when the Ni/(Fe + Ni) is low, the color of the clay is pale and yellowish. The S content of the clays also varies from below the detection to 66,000 ppm but does not show any correlation with the Ni/(Fe + Ni) ratio. Some clays have an extremely PGE- and Au-enriched feature, and the IPGE concentration is 100 times higher than the chondrite values. The presence of high-Ni halo and chemical zoning of NiO content of olivine from the center (5.3 wt%) to the outward (0.4 wt%) in the Ni-rich domain, the high-Fe, -Ni, -S clays are an alteration product of the metasomatic agent that drastically enhanced the Ni content of the surrounding minerals. We propose these clays were new type of S-rich silicate melt or silicate-bearing aqueous fluid to concentrate PGE and Au in addition to Ni and Fe within the mantle wedge.

[1] Ishimaru & Arai (2008) *CMP* **156**, 119-131.

## Processes and timescale of subduction initiation and subsequent evolution of oceanic island arc

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The Izu-Bonin-Mariana (IBM) forearc is thought to be an excellent location for investigating the record of subduction initiation and subsequent arc evolution [1] because of the exposure of early-arc lavas on the forearc islands. Recent dredging and diving in the IBM forearc [2, 3] have revealed a bottom to top stratigraphy of: 1) mantle peridotite, 2) gabbroic rocks, 3) a sheeted dyke complex, 4) basaltic pillow lavas (forearc basalts: FAB), 5) boninites and magnesian andesites, 6) tholeiites and calcalkaline arc lavas. This forearc stratigraphy is remarkably similar to that found in many ophiolites.

The FAB and associated diabase overlying gabbros can be regarded as a first magmatic product produced by decompression melting associated with subduction initiation. <sup>40</sup>Ar/<sup>39</sup>Ar ages of 48-52 Ma for these basalts as well as 51.6-51.7 Ma zircon U-Pb ages for the gabbros strongly imply that subduction initiation took place at 51-52 Ma. The change to flux melting and boninitic volcanism took 2-4 m.y., and the change to flux melting in counterflowing mantle and "Normal" arc magmatism took 7-8 m.y. This evolution from subduction initiation to arc normalcy occurred nearly simultaneously along the entire length of the IBM subduction system. The contemporaneity of IBM forearc magmatism with the major change in plate motion in Western Pacific at ca. 50 Ma suggests that the two events are intimately linked. Mesozoic rocks found in the deep Bonin forearc suggest that the overriding plate at subduction initiation consisted of Mesozoic terranes.

The similarity between the IBM forearc stratigraphy and many ophiolites supports the hypothesis that the forearc crust section that is produced at subduction initiation and is preserved in the IBM system represents an in-situ section of supra-subduction zone ophiolite.

[1] Stern & Bloomer (1992) *Geol. Soc. Am. Bull.* **104**, 1621-36. [2] Reagan *et al.* (2010) *G<sup>3</sup>*, doi:10.1029/2009GC002871.

[3] Ishizuka *et al.* (2011) *Earth Planet. Sci. Lett.* **306**, 229-240

## Organic geochemical analysis of the impact of cadaver burial on soil

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A comparative study of soil lipids collected from eleven crime scenes across Malaysia, with different post-depositional intervals (PDI) of cadavers, was conducted. A laboratory degradation study of porcine flesh in soil was also carried out in parallel. The overall premise for this work was that organic molecular components in soil will be useful in determining the provenance of a cadaver and/or calculation of its post-mortem interval (PMI).

The results from the Malaysian samples show that the concentrations of palmitic (C16:0) and stearic (C18:0) acids are higher in the cases with a low PMI. In addition, their unsaturated analogues, palmitoleic (C16:1) and oleic (C18:1) acids are also present at high concentration. The higher concentration of cholest-5-en-3 $\beta$ -ol (cholesterol) in the cases with low PMIs indicates that this component is most likely derived from the decomposing body. The cases with longer PDI demonstrate a large shift towards plant-derived organic material. Differences observed are presumably due to the transformation of the cadaver derived lipids and can be associated with PMI and/or PDI.

Subsequently, porcine flesh was degraded in aerobic and anaerobic soil mesocosms, representative of tropical and temperate climates, for a year. Mesocosms were sampled throughout the experiment and target analytes were chosen to provide information about both materials derived from the flesh and the response of the microbial community to its presence in the soil environment. Initial results reveal that flesh derived triacylglycerol components degrade within the first 120 days resulting in a corresponding increase in concentration of free fatty acids, i.e. palmitic and stearic acids. Similar patterns of degradation are observed under both aerobic and anaerobic conditions. Preliminary analysis of phospholipid fatty acid distributions, derived from the soils, reveals a concentration increase in the region of 180-400% for soils incubated with porcine flesh after 121 days, with a currently unidentified C18:1 fatty acid moiety becoming the dominant component in the latter samples.

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## Role of acid mobilization in association of smaller particle size with higher iron solubility

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Iron (Fe) is an essential nutrient for phytoplankton. Iron-containing soil dust mobilized from arid regions supplies the majority of iron to the oceans, but primarily presents in an insoluble form. Since most aquatic organisms can take up iron only in the dissolved form, a key flux is the amount of soluble iron in terms of the biogeochemical response to atmospheric deposition. Atmospheric processing of mineral aerosols by anthropogenic pollutants may transform insoluble iron into soluble forms. We discuss the effect of the acid mobilization on a relationship between aerosol iron solubility and mineral particle size in an aerosol chemistry transport model [1]. The iron solubility from onboard cruise measurements [2, 3] over the Atlantic and Pacific Oceans in 2001 is used to evaluate the model performance in simulating soluble iron.

The association of smaller size with higher solubility as a role of the acid mobilization considerably improves the results of soluble iron in terms of ratio of fine to total particles, compared to constant iron solubility. The improvement of model-observation agreement provides strong evidence for faster iron dissolution in fine particles by anthropogenic pollutants. Accurate simulation of the ratio of fine to total aerosols of soluble iron has important implications with regards to the ocean fertilization because of a longer residence time of smaller particles, which supply nutrients to more remote ocean biome. The model reveals higher concentration of soluble iron in the coarse mode than that in the fine mode over the Southern Ocean except downwind regions of Australian dust, in contrast to the Northern Ocean. These results suggest that dust does not efficiently transport soluble iron to significant portions of the Southern Ocean. This corroborates hypothesis that phytoplankton blooms are not sustained by the supply of iron to surface waters from dust deposition in the Southern Ocean [4] except the Australian sector [5].

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## Zircon U-Pb and FT dating on clastic dykes in the Matsukawa Geothermal field, Japan, with reference to the Quaternary Kakkonda granite

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We have determined both U-Pb and fission-track (FT) zircon ages from Quaternary clastic dykes in the Matsukawa Geothermal field, northeast Japan [1]. Since the dykes contain granitic xenoliths, the dated zircons may have derived from granitic basements underneath. A weighted mean LA-ICP-MS U-Pb (<sup>238</sup>U-<sup>206</sup>Pb) age of 1.30±0.04 Ma (1σ error) and a weighted mean FT age of 1.0±0.1 Ma (1σ error) were obtained from the zircons. This indicates that if zircons are of granitic origin, the granite intruded ~1.3 Ma and cooled to ~300 °C at ~1.0 Ma, considering closure temperatures of both the dating methods.

Adjacent to the Matsukawa geothermal area, the Quaternary Kakkonda granite with K-Ar ages of 0-0.2 Ma resides below 1.5-3 km depths. The intrusion of the Kakkonda granite is assumed to be ~1.0 Ma based on geological and geochronological evidence [2]. Therefore strong correlation is plausible between the two granites.

U-Pb zircon dating of the Kakkonda granite is now under way. We will report the dating results and the relevance of the Quaternary granite for the related geothermal systems.

Sample code	Number of grains	Dosimeter number	Dosimeter density x 10 <sup>4</sup> cm <sup>-2</sup>	Spontaneous number	Spontaneous density x 10 <sup>5</sup> cm <sup>-2</sup>	Induced number	Induced density x 10 <sup>6</sup> cm <sup>-2</sup>	P(χ <sup>2</sup> ) %	T ± 1σ Ma
SP-2	30	2270	3.487	88	1.27	2096	3.03	75	1.0 ± 0.1

Ages are calculated using  $\lambda_{238} = 142.1 \pm 5.7$  (1σ error). Dosimeter glass CN-1 used.

**Table 1:** Zircon fission-track dating result.

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## Two flood basalt events and contemporary granites within the same LIP: Siberian Traps case study

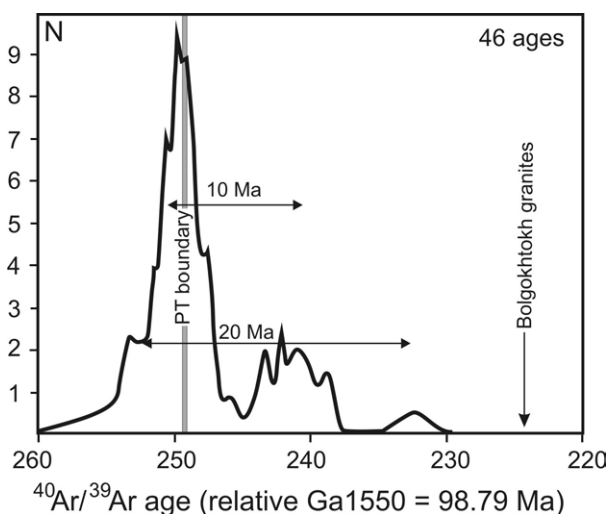
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Siberian Traps LIP contains effusive, intrusive and volcanoclastic rocks of variable composition from ultrabasic to acidic, though low-Ti basalts and their intrusive analogues are predominant rock types. Our new <sup>40</sup>Ar/<sup>39</sup>Ar results combined with published values suggest that basaltic magmatism appeared during different periods of time (Fig. 1). Among four episodes, at least two (at the Permo-Triassic boundary and one at the Early/Middle Triassic) can be considered as flood basalt events on merit of the volume and geochemistry. Two other episodes of basaltic volcanism were probably less voluminous. U-Pb data for granites show that granites in peripheral parts of the Siberian Traps LIP were contemporaneous to the two flood basalt events, but the latest Bolgokhtokh intrusion is younger than any of basalt. Thus Siberian Traps LIP is much more complex than usually considered.



**Figure 1:** Probability distribution of <sup>40</sup>Ar/<sup>39</sup>Ar ages.

## Fluid processes in subduction zones and global water circulation

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Water within the Earth, including OH and H in minerals, may play an important role in the planetary evolution, yet its distribution and circulation are poorly constrained. Seismic observations, e.g., those based on dense networks over the Japan arcs, suggest deep subduction of water and dehydration of the slab [1 and the refs. therein]. Geochemistry of volcanic rocks is useful for quantifying the amount and composition of slab-derived fluid, and suggests a typical range from 0.1 to 1 wt.% H<sub>2</sub>O in the mantle wedge with regional variations according to the tectonic settings [2]. Numerical models provide a consistent view, in which fluid flow with local chemical equilibration explains the above observations [3]. In addition, these models and water solubility to minerals at high pressures [4] imply that a boundary layer with several 1000 ppm H<sub>2</sub>O hosted by NAMs subducts to depths greater than 300 km.

The deeply subducted water, especially in the lower mantle, is not well mapped by geophysical means: seismic velocity may be influenced by major element compositions and temperature, while electrical conductivity is sensitive to the amount of water but provides a poor spatial resolution at depths [5]. Geochemistry of oceanic basalts can be used as a probe for the subducted components. Statistical analysis on the mantle isotopic variability suggests that such a component is in fact inherited in the mantle and forms geographical domains, possibly related to the extensive subduction having surrounded the supercontinents in the past, Pangea, Gondwana and Rodinia [6]. Repeated formation-breakup of supercontinents seems to be recorded in the mantle geochemistry, controlling the global material circulation.

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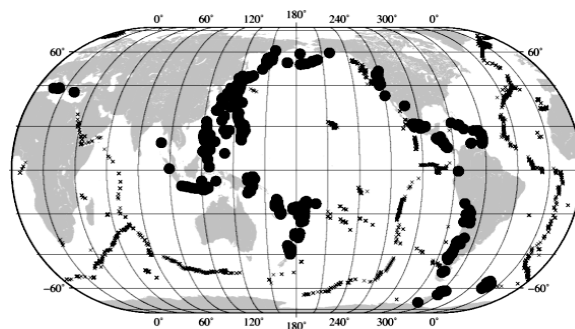
## Mantle compositional variability constrained from arc and oceanic basalts

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Mantle compositional variability has been extensively studied using oceanic basalts, including mid-ocean ridge basalts (MORB) and ocean island basalts (OIB), as geochemical 'messages' from the mantle [1]. However, the spatial coverage of ridges and ocean islands is insufficient for resolving even a global distribution of compositional variability (Fig.1). Here we discuss the mantle compositional variability in subduction zones that extend over a long distance comparable to mid-ocean ridges, mostly around the Pacific Ocean (Fig.1). As a result, we are able to map global geochemical domains, when combined with the mantle compositional variability obtained from MORB and OIB.

Arc basalts associated with subduction are the products of interaction between slab-derived materials and mantle wedge beneath the arcs. In order to extract the compositional variability of the mantle, influence of the subducted materials needs to be evaluated. Based on Sr, Nd and Pb isotope ratios mainly from the GEOROC and PetDB databases, and using the multivariate analyses, in particular, Independent Component Analysis, it has been found that depleted portions of the arc basalts well represent the compositions of mantle wedge that has not been fluxed by slab-derived materials. These portions lie on a compositional plane that is well defined by MORB and OIB, and can be decomposed into two independent components. Consequently, geographical domains in terms of 'anciently subducted component' ('IC2' in [2]) have been found and its implications on mantle dynamics are discussed.



**Figure 1:** Distribution of oceanic basalts (small crosses) and arc basalts (solid circles) used in this study.

[1] Hofmann (1997) *Nature* **385**, 219-229. [2] Iwamori *et al.* (2010) *EPSL* **229**, 339-351.

## $\delta^{13}\text{C}$ evidence of conodont evolution as a response to bioproduction perturbations

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Usually  $\delta^{13}\text{C}$  variations in marine sediments are related to the mass extinction in the Earth's past, and explained as reflection of the changes in primary bioproduction of the paleoceans, but sometimes the  $\delta^{13}\text{C}$  excursion coincide with important evolutionary changes in biosphere. One of examples is radiation of polygnathid conodonts at the lower Emsian (Devonian), where negative  $\delta^{13}\text{C}$  excursion (from +2 to -0.7 ‰) is aligned with the appearance of well-developed Pa element of the *Polygnathus kitabicus*, *Pol. panonicus* and *Pol. sokolovi*.

Apart of bioproduction decrease, carbonates secondary changes also may cause negative excursion. To exclude the diagenetic nature of these isotopic signals, investigations of geochemical criteria of primary carbonate material safety (Fe/Sr and Mn/Sr) have been done. Together with the petrographic studies they are very effective for allocation of diagenetically altered samples.

All studied lower Emsian samples from Zinzilban section (Zeravshan Ridge, Kitab State Geological Reserve, Uzbekistan) are characterized by the low concentration of Fe (<100 ppm) and Mn (<22 ppm) with Sr contents from 150 to 400 ppm. Thus, Fe/Sr and Mn/Sr not exceed 0.5 and 0.07 accordingly, that evidence absence of carbonate material alteration. Also, it was controlled by petrographic studies. Thus,  $\delta^{13}\text{C}$  negative excursion with high probability is a primary signal and the correlation of this event with the complication of conodont Pa element can reflect changes in their nutrition type, induced by the decreasing of the simple food.

## Mo-isotopes as tracers of Cretaceous ocean anoxia

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Recent observations and modelling have shown that ocean warming and stagnation, driven by global climate change, may lead to widespread ocean deoxygenation with direct impacts on marine biogeochemistry and ecosystems. Measurements of marine oxygen levels extend back no more than c. 50 years, whilst accurate predictions of future deoxygenation trends are difficult and uncertain. In contrast, the geological record of past abrupt global warming events can provide insights into the entire earth system response - the mechanisms, extent, duration and consequences of - seawater deoxygenation that are associated with CO<sub>2</sub>-induced global warming.

The Cretaceous oceans were particularly susceptible to transient widespread deoxygenation, containing as many as 6 discrete intervals known as Ocean Anoxic Events (OAEs). Of these, OAE 1a (~120 Ma) and OAE 2 (~93 Ma) may have been global in extent and are marked by a sudden increase in organic C accumulation in conjunction with broad positive carbon isotope excursions.

We present new Mo-isotope, trace element and Fe-speciation analyses of samples from OAE 1a (the Selli event) and OAE 2 (the Bonarelli Event). Mo-isotope data can, under certain circumstances, provide quantitative estimates of how the extent of seawater anoxia may have fluctuated in the past. Our data from Gorgo a Cerbera, Italy, indicate that local conditions became progressively more reducing during OAE1a.  $\delta^{98/95}\text{Mo}$  ratios show pronounced stratigraphic variations, consistent with diminished oxic sedimentation globally. Laminated sediments from Demerara Rise are enriched in redox sensitive trace metals (RSTM) throughout much of the Cenomanian. However, OAE 2 is marked by relatively low levels of RSTM consistent with the global expansion of anoxic sedimentation and the drawdown of the RSTM inventory. Our sample specific Fe-speciation data show that the water column was periodically euxinic, allowing us to use Mo-isotope data to critically test ideas on the timing, extent and duration of one of the most pronounced deoxygenation events of the Mesozoic.