

## Experimental and modeling studies of CO<sub>2</sub>-water-rock interactions in the Rio Bonito saline aquifer, Paraná Basin, Brazil

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Geological storage of CO<sub>2</sub> is one of the most promising solutions for climate change mitigation. CO<sub>2</sub> captured from large stationary sources such as coal-fired power plants, oil refineries and industries, can be safely injected and stored in appropriate geological formations, such as mature oil fields, unmineable coal deposits and saline aquifers.

Here we report an experimental and modeling study of CO<sub>2</sub>-water-rock interactions of subarkose Permian sandstones from the Rio Bonito Formation aquifer, in the Paraná Basin, Brazil. These sandstones are the most promising reservoirs for geological storage in Brazil, owing to the good reservoir quality (high porosity and permeability), adequate depth (more than 800 m), occurrence of high salinity formation water (> 10.000 mg/L) and the proximity of large stationary CO<sub>2</sub> sources in the south and southeast of Brazil. This work aims to study the mineralogical integrity of the Rio Bonito sandstone reservoirs, analysing the dissolution of original minerals and precipitation of carbonate mineral phases resulting from the reaction with supercritical CO<sub>2</sub>.

Experiments were performed in a stainless steel batch reactor, equipped with pressure meter and temperature control. Three sandstone samples were reacted separately with deionized water and CO<sub>2</sub> (added as dry ice), in a 5:80:105 m/m ratio. The system was allowed to react continuously for 100 h. To increase the reaction rates, higher temperature than expected for reservoir conditions was employed (200°C). Pressure reached a maximum of 100 bars. Sandstone samples were dried in a desiccator and characterized by Scanning Electron Microscopy (SEM) before and after the reactions. Results of the study indicated the dissolution of K-feldspars and carbonates. Calcium and iron carbonate (CaCO<sub>3</sub> and FeCO<sub>3</sub>), calcium sulfate, kaolinite, and silica precipitation was observed, as an evidence of pyrite and K-feldspar alterations.

Geochemical modeling of the reactions was carried out using the PHREEQC code V2.8. Equilibrium and kinetic batch modeling of the reacting system was performed. Results are in agreement with the observed dissolution/precipitation behaviour of the minerals in the experiments.

## Penetrative convection in Earth's mantle: Reconciling geophysical and geochemical perspectives on mantle structure and evolution

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The nature of mantle convection continues to be the subject of debate. Geochemical observations of mantle-derived magmas suggest that globally distributed reservoirs with relatively uniform composition exist within the mantle. These data have led to Earth models that call for layered chemical shells with minimal exchange of material occurring between them. Yet, geophysical observations indicate that large circulation cells span the entire depth of the mantle and seem to obviate long-standing, compositionally distinct layers in Earth's mantle. Here, a penetrative convection model is revisited and expanded upon to reconcile these alternative explanations. The model calls for independent layered reservoirs whereby passive material transfer is inhibited by the endothermic phase transition occurring at 660 km depth. The upper mantle consists of rapidly circulating, well-mixed material that is continually depleted in incompatible and volatile elements via formation of oceanic and continental crust. The lower mantle is composed of independently circulating material that is shielded from chemical fractionation processes. Only material originating from thermal boundary layers as part of the large scale convective flow (slabs and plumes) may penetrate the boundary between the two reservoirs. The dense Ca, Al-rich (Mg-poor) basaltic fractions of penetrating slabs descend to D'' and remain chemically isolated from the overlying lower mantle. The less dense, Mg-rich (Ca, Al-poor) fractions of penetrating slabs mix into the lower mantle, imparting a depleted character to the otherwise undegassed reservoir. Upwelling plumes originate in D'' and rise to the base of the lithosphere to produce hotspot magmas with the character of recycled oceanic crust. Some lower mantle material is entrained into every upwelling plume, imparting an undegassed component (FOZO) to all hotspot magmas. The phase transition serves to regulate both material and heat transfer across the boundary, and the transition should naturally evolve to a depth that will allow only a fraction of slabs to penetrate into the lower mantle (as observed today). The penetrative convection model is consistent with first-order geophysical and geochemical observations of Earth's mantle.

## Tungsten isotopic investigation of Eoarchean terrestrial rocks with implications for mantle evolution

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Young terrestrial rock samples exhibit a  $\epsilon^{182}\text{W}$  that is  $\sim 2\epsilon$  higher than that of chondrites. The  $^{182}\text{W}$  excess has been used to infer the timing of core-separation, by assuming that the  $\epsilon^{182}\text{W}$  for the samples are representative of those for the bulk silicate Earth at the time of core formation. However, this assumption may not be valid for the following two reasons. (i) Mixing of core material back into the mantle could change  $\epsilon^{182}\text{W}$  of the mantle with geological time. Indeed, a grain-boundary diffusion study [1] indicates that W mobility is high enough to allow significant core-mantle interaction, especially if material diffused into the lowermost mantle is swept into the mantle convection. (ii) The superchondritic  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios for all terrestrial rocks analyzed so far suggest the presence of an early-formed enriched reservoir (EER) that has never participated in surface volcanism. If the hidden EER was formed during the lifetime of  $^{182}\text{Hf}$  (in the first  $\sim 60$  Myr of the solar system) as proposed by the  $^{142}\text{Nd}$ - $^{143}\text{Nd}$  isotope systematics [2], the EER will have lower  $\epsilon^{182}\text{W}$  relative to the known terrestrial rocks due to the high incompatibility of W relative to Hf during mantle melting.

To constrain W isotopic evolution of the Earth's mantle, we studied Eoarchean meta-igneous rocks from the Isua greenstone belt (3.8–3.7 Ga) and Acasta Gneiss Complex (4.0–3.6 Ga). The Isua rocks display a  $^{142}\text{Nd}$  excess of 11 ppm relative to modern upper mantle composition [3], suggesting the heterogeneity of the  $^{142}\text{Nd}/^{144}\text{Nd}$  within the early depleted reservoir (EDR) that is complementary to the EER. Our data reveal that  $\epsilon^{182}\text{W}$  in the analyzed samples are uniform within analytical uncertainties ( $\pm 0.3\epsilon$ ), and indistinguishable from the modern mantle signatures, suggesting that the  $\epsilon^{182}\text{W}$  of the upper mantle has not changed from the Eoarchean to the present. These results imply that the lowermost mantle involving W from the core has isolated from the mantle convective cycling and that a silicate fractionation causing the  $^{142}\text{Nd}/^{144}\text{Nd}$  heterogeneity within the EDR occurred after  $^{182}\text{Hf}$  became extinct.

[1] Hayden & Watson (2007) *Nature* **450**, 709–711. [2] Boyet & Carlson (2005) *Science* **309**, 576–581. [3] Caro *et al.* (2006) *GCA* **70**, 164–191.

## Controls on antimony and arsenic speciation via sorption and redox chemistry at the clay mineral – water interface

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Antimony (Sb) and arsenic (As), both toxic metalloids, pose a potential threat to aquatic systems and water quality throughout the world. The mobility of these metalloids is controlled to a large extent by adsorption and redox reactions at mineral surfaces, including Fe, Al and Mn oxides, and clay minerals, that find widespread occurrence in low-temperature settings. The extent of As and Sb adsorption depends on a number of variables including, oxidation state (+5/+3), physicochemical conditions, type of surface moieties available for reaction, and presence or absence of effective electron donor/acceptor species. Our primary motive in this study is to investigate the potential for heterogeneous redox in clay dominated systems with variable composition and at variable redox potential.

Batch measurements of the rate and extent of arsenic and antimony sorption to iron-rich nontronite clay (NAu-1) were coupled with spectroscopic analysis of the sorption products using X-ray absorption spectroscopy (XAS). Reduced and oxidized forms of nontronite clay were equilibrated with As(III/V), and Sb(III/V) solutions under anoxic conditions, with UV light excluded. Additional measurements were performed in the presence of soluble Fe(II). Synthetic hydrous Al oxide with As(III/V), Sb(III/V) adsorbed were examined as non-redox control samples. The extent of adsorption, speciation and local bonding environment of arsenic and antimony on iron rich nontronite clay will be discussed along with the significance for the environmental cycling of As and Sb.

## Reaction of aqueous U(VI) with nano-crystalline magnetite

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U(VI)aq was reacted with nano-crystalline magnetite for 1-9 weeks at pH 5-5.4. Solid run products were analyzed with high resolution X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption spectroscopy (EXAFS). XPS indicated the presence of both U(VI) and U(V) on the near surface of magnetite. This contrasts strongly with the interaction of U(VI)aq with green rust, where XPS analyses were consistent with near-stoichiometric UO<sub>2</sub> on the surface. EXAFS indicated the presence of a uranyl species with axial bond lengths around 1.8 Å and a species with U-O bond lengths at 2.05 Å, which we shall call the uranate species. An analysis of second nearest neighbours EXAFS indicated the presence of relatively large multiple Fe shells at distances between about 3.5 and 4.3 Å. Second neighbour U were inconsistent with the EXAFS data. We initially conclude that at least two U species are present, including surface-bound U(VI) and uranium incorporated into a Fe-oxide phase, possibly a surface alteration product. The putative incorporation site is not compatible with the Fe1 or Fe2 sites of magnetite. The uranate phase is consistent with either U(VI) or U(V), but certainly not U(IV). These results suggest that the uranate phase reflects a reductive environment and could in fact be the U(V) species identified by XPS. If this is the case, then the experiments provide the first evidence that U(V) can be stabilized on or near a mineral surface at low sorption densities during heterogeneous reduction of U(VI)aq.

## Coal-based seafloor seep microbial ecosystem

FUMIO INAGAKI, YUKI MORONO, AND “CHIKYU” SHAKEDOWN EXPEDITION CK06-06 SCIENTIFIC PARTY

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Recent studies of the deep seafloor biosphere have suggested that microbial population and activities in sediments are controlled by nutrient and energy flux(s) transported via the overlying seawater and/or the secondary seawater circulation through the basaltic aquifer [1]. The microbial populations in marine sediments generally decrease with increasing depth [2], except for sedimentological and geochemical interfaces, and the metabolic activities and turn over rates are extremely low. The available nutrient and energy sources are subsequently limited in deeper sediments with burial, hence the adaptation of long-term survival as well as the dynamics of population and activities corresponding to the energy and nutrient fluxes in the deep seafloor biosphere remain largely unknown.

From August to October in 2006, the newly constructed deep-sea drilling research vessel “Chikyu” went down on the shake down cruise CK06-06 offshore the Shimokita Peninsula, Japan. During the expedition, a 365 m-sediment core was recovered from a methane hydrate field, where the presence of thick coal layers (TOC 40-60%, 30-125 m in thickness) was expected at around 2,000 mbsf by the preliminary multiple seismic profiles [3] and the previous drilling survey of natural gas production [4]. The thick coal layers produce large amount of hydrocarbon gases via physical and/or biological degradation processes *in situ*, from which derived carbon components, as well as some other nutrient and energy substrates such as nitrogen sources, are transported upward through the sediment column via fluids and gas flows, which may support active and abundant microbial habitat in the deep marine subsurface. We will show microbiological and biogeochemical characteristics of the sediment core off Shimokita, and will discuss about the nature of seafloor life in the coal-based seafloor seep ecosystem.

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## Water diffusion in forsterite revisited

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Protons influence strongly the diffusion of atomic species in olivine and affect its deformation properties at high temperature [1, 2, 3]. But, even for pure forsterite, the nature of hydrogen defects is still a matter of debate; two main defects have been proposed: one involves metal vacancies in octahedral sites and is linked to OH infrared bands appearing in the range of 3100-3200 cm<sup>-1</sup> and the other involves silicon vacancies in tetrahedral sites with OH infrared bands around 3600 cm<sup>-1</sup>. Their mobility depends on the diffusivity of hydrogen atoms and the diffusivity of octahedral and tetrahedral vacancies, respectively. We measured the mobility of these two defects from chemical hydrogen diffusion experiments performed in synthetic forsterite between 800 and 1000°C [4]. We used forsterite single crystals, synthesized by Lemaire *et al.* [5] at different silica activities, containing the two types of OH defects. We compare our results with hydrogen “self-diffusion” data and we discuss their implication in term of transport properties in forsterite.

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## Redox condition *in situ* survey around the underground rock cavern

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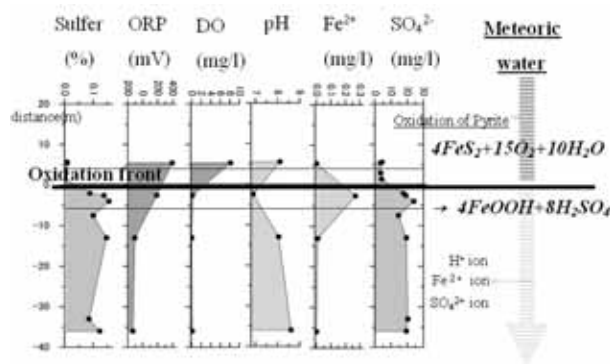
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### Introduction

The investigation and the evaluation of the redox condition around the underground rock cavern are considered an important item in the safety assessment to the sub-surface geological disposal of the radioactive wastes. In this report, some redox condition *in situ* surveys are carried out around the investigation cavern excavated in the Neogene pyroclastic rocks.

### Consequence

The chemical analysis of the rock [1, 2], the chemical analysis of the pore water [3] discharging into a small hole bored by the portable rock drill, and the microbial community analysis [4] around the oxidation front distributing above the cavern are conducted. Pyrite included in rocks is thought to oxidize by the oxygen dissolved in the groundwater infiltrating from the surface.



[1] Oyama T. *et al.* (2007) Japan Geoscience Union Meeting. [2] Oyama T. *et al.* (2007) *CRIEPI Rep.* N07001. [3] Inohara Y. *et al.* (2007) Annual study meeting, JSEG. [4] Nagaoka T. *et al.* (2007) Annual meeting of AESJ.

## Geochemical fingerprinting of the lithospheric mantle using high-precision olivine analyses

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Olivine is the dominant mineral in the lithospheric mantle. Worldwide compilations of Mg# [ $\text{Mg}/(\text{Mg}+\text{Fe})_{\text{ol}}$ ] and minor components in olivine generally show broad scatter related to low precision of routine electron probe data and complexities of mantle processes. We have obtained high-precision Mg# and abundances of Ni, Mn, Co, Ca, Al and Cr in olivine from ~400 mantle peridotites on a Jeol JXA8200 electron probe using high sample current, extended counting time and continuous monitoring [1]. Trace element abundances in olivines were obtained by laser ablation ICPMS. The samples are xenoliths in basalts, andesites and kimberlites as well as abyssal and massif peridotites with a broad range of modal, major- and trace-element whole-rock compositions.

Spinel peridotite xenoliths in intra-plate basalts, abyssal and massif peridotites that show little or no metasomatism (i.e. no volatile-bearing minerals and no Fe-enrichments [2]) define a negative linear trend ( $r^2 \sim 0.97$ ) on a Mg#-MnO plot from  $\text{Mg\#}_{\text{ol}} \sim 0.891$  and  $\text{MnO}_{\text{ol}} \sim 0.148\%$  to  $\text{Mg\#}_{\text{ol}} \sim 0.922$  and  $\text{MnO}_{\text{ol}} \sim 0.115\%$ , with  $\text{Fe}/\text{Mn}_{\text{ol}}$  decreasing from 72 to 68. The positive Mg#-NiO correlation is poor ( $r^2 \sim 0.45$ ), possibly due to Ni partitioning to sulfides. Olivine in the most fertile garnet lherzolites (8-12% garnet) has higher Mg# (0.898) and Fe/Mn (75-81) and lower MnO (0.127%) than olivine in the most fertile spinel lherzolites due to preferential partitioning of Fe and Mn to garnet. Olivine in metasomatised spinel peridotites tends to have higher MnO and lower Fe/Mn (60-68) at given Mg# than for melting residues. Ca abundances are positively correlated to temperature and define a good geothermometer. The contents of incompatible trace elements in olivine decrease from fertile to refractory rocks, but olivine in garnet peridotites contains more Ti, V, Zr, Cu, Zn than in spinel peridotites. Overall, high-precision olivine analyses may constrain degrees and conditions of partial melting and/or metasomatism, tectonic settings, modal compositions and equilibration conditions of mantle peridotites.

[1] Sobolev *et al.* (2005) *Nature* **434**, 590-597. [2] Ionov (2007) *CMP* **154**, 455-477.

## Highly siderophile elements and $^{187}\text{Os}/^{188}\text{Os}$ in the parental melts of Hawaiian picrites

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Absolute and relative abundances of the highly siderophile elements (HSE: including Os, Ir, Ru, Pt, Pd and Re) were measured in 54 Hawaiian picrites (MgO >13 wt%) and 6 tholeiitic basalts (~7 to 12 wt% MgO) from nine volcanic centers (Mauna Kea, Mauna Loa, Hualalai, Loihi, Koolau, Kilauea, Kohala, Lanai and Honomanu). The parental melts for all the volcanic centers are estimated to contain ~16 wt% MgO. Samples with higher MgO contents contain accumulated olivine. Samples with lower MgO contents have lost olivine.

The HSE abundances for the parental melts of each volcanic center are estimated by consideration of the intersections of HSE-MgO trends with 16 wt% MgO. The estimated HSE abundances in the parental melts of most of the volcanic centers are very similar:  $0.5 \pm 0.2$  ppb Os,  $0.45 \pm 0.05$  ppb Ir,  $1.2 \pm 0.2$  ppb Ru,  $2.3 \pm 0.2$  ppb Pt, and  $0.35 \pm 0.05$  ppb Re. All Hualalai samples contain higher absolute abundances of Os, suggesting a parental melt with ~1.1 ppb Os. This difference is the only hint of a discernible HSE heterogeneity that can potentially be linked to the mantle source. Effects of crustal contamination and volatile losses on parental melt compositions were likely minor, except for Re and possibly Ir.

Two types of HSE patterns are observed among the various picrites. One type of pattern is characterized by greater fractionation between Os, Ir, Ru versus Pt and Pd, with higher Pt/Ir and Pd/Ir ratios compared to the other type of pattern. Both pattern types are present in most of the volcanic centers. The differences between the two patterns are attributed to the inter-relationship between partial melting and crystal-liquid fractionation processes, and mirror both differences in residual sulfides and the loss of sulfides during magma ascent. These residual sulfides mask any source heterogeneities in terms of HSE.

The  $^{187}\text{Os}/^{188}\text{Os}$  ratios of our suite of picrites range from ~0.129 (Mauna Kea) to ~0.138 (Lanai). There is no resolvable correlation between  $^{187}\text{Os}/^{188}\text{Os}$  and Os (or other HSE) abundance estimated for parental melts, as might be expected if isotopic variations reflect the presence of variable proportions of recycled oceanic crust added to a common source, as has been commonly proposed.

## The chemistry of isotopic anomalies

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Isotopic anomalies can give us direct insight into stellar nucleosynthesis. However, we are presented with a very biased view of nucleosynthetic inputs because of the differing chemical characteristics of the elements. We are in fact presented with isotopic anomalies primarily in the most volatile and most refractory of elements.

Noble gases are widely regarded as anomalous in almost every context of the solar system. Many components are apparent from many sources. Despite their lack of reactivity, the components have remained isolated through the formation of the solar system. While this is not surprising in the case of preservation in presolar grains, large abundance variations on Earth suggest preservation of a variety of components even on a planet that remains geologically active.

Isotopic anomalies in refractory inclusions are ubiquitous. Calcium and titanium anomalies can be especially large. However, their preservation in chemically and petrologically different objects suggests that a variety of different processes are active and care must be taken to isolate the relevant signatures. The most anomalous inclusions have REE abundances that are near chondritic suggesting that at least two refractory inventories are involved, one being a Ca-Ti-Al oxide, the other carrying heavier refractory elements in chondritic abundances. Fractionation of the REE according to volatility is a key parameter in the early solar system, and remains one of the outstanding issues in cosmochemistry. Inclusions carrying this chemical signature appear to show less variation in their isotopic components.

Oxygen is a special case in many ways. It exists in both volatile (e.g. CO) and refractory species (e.g. Al<sub>2</sub>O<sub>3</sub>) and so covers the entire condensation sequence. While isotopic anomalies are apparent in presolar oxide grains, the isotopic signature in the solar system is dominantly one of chemical fractionation that affected the abundance of the major isotope <sup>16</sup>O. While molecular symmetry plays a role in the oxygen abundances of ozone in the stratosphere, such a scenario probably has a more limited role in the early solar system. Rather, a scenario based on photodissociation of CO is favoured whereby UV photons discriminate the isotopes with optical depth. The key ingredient for determining the processes responsible for oxygen isotope fractionation in the early solar system is the solar composition because it represents the initial state of the nebula.

## Evidence for sulfur-rich fluids in the ancient angrite parent body

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Angrite meteorites (now totaling 12 specimens) have non-correlated relative abundances of elements of differing geochemical behavior [1]. Despite relative enrichment in refractory elements (e.g., Ca, Ti) and extreme depletion in moderately volatile elements (e.g., Na, K, Li, Rb, Cs, Mn, Ga), angrites are surprisingly *not* very depleted in highly volatile elements (e.g., S, Se, Br, Zn, Cd, In). Additionally, even though all angrites contain Fe metal, the recent discovery of ferric iron-bearing rhönite in NWA 4590 [2], coupled with lack of evidence for ferric iron-bearing silicates in metal-rich angrite NWA 2999, suggest that the redox state within the APB may be quite variable (perhaps from IW to IW+2). By analogy with the chemical and mineralogical features of terrestrial lithospheric mantle xenoliths (e.g., [3]), the chemical attributes of angrites likewise may imply interaction of primary angrite assemblages with subsequent migratory metasomatic fluids (but, unlike on Earth, anhydrous ones).

Elemental mass balance calculations for the phases within the symplectites and coronas prevalent in NWA 2999 [4, 5] indicate that Ti and Cr were mobile during the non-isochemical, solid-solid reactions responsible for formation of these disequilibrium microstructures. The relative abundance of accessory troilite (with metal) and the chalcophile element enrichment in angrites suggest that such metasomatism may have been facilitated by sulfur-rich fluids (perhaps rich in S-O or sulfide species). The vesicles and vugs prevalent in some angrites also dictate that a free vapor phase existed.

Oxygen isotopic compositions by laser fluorination for acid-washed samples of NWA 4801 are:  $\delta^{17}\text{O} = 1.809, 1.823$ ;  $\delta^{18}\text{O} = 3.595, 3.544$ ;  $\Delta^{17}\text{O} = -0.082, -0.041$  per mil. These results extend  $\delta^{18}\text{O}$  for analyzed angrites to lower values, giving a data array subparallel to the TFL (as for known planetary meteorites).

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## Subseafloor phase separation and fluid migration supports *Calyptogen* colony in the marginal region of a hydrothermal field

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In the Iheya North Knoll hydrothermal field in the mid-Okinawa Trough (27°47.5'N, 126°53.8'E, depth=1000m), high temperature clear fluid (T=311°C) is vigorously venting from a giant mound structure (named as NBC). Benthic colonies are found not only around the mound, but also in the marginal part of the hydrothermal field; for example a *Calyptogen* colony at 200m east and a tube-worm colony at 250m southeast from the NBC mound.

During Leg 3 of KY05-14 cruise (R/V *Kaiyo* of JAMSTEC) in January 2005, we conducted pinpoint piston coring using a newly developed ROV "NSS (Navigable Sampling System)" that installs a monitor camera and thrusters. Two cores were successfully collected with length of about one meter from the benthic colonies.

Pore fluid in the surface pumiceous sediment collected from the *Calyptogen* colony showed unusual chemistry characterized as low chloride, low magnesium, and high methane concentrations. Lower Na/Cl ratio than seawater and <sup>13</sup>C-depleted methane isotopic composition were close to those of the high temperature fluid venting from the NBC mound. These results strongly suggest contribution of a vapor-rich hydrothermal component into the pore fluid, which migrates within the sediment layer from the central mound 200 meters away.

Moreover, notable decrease of sulphate concentration accompanied by increase of alkalinity was found even in the surface pore fluid less than one meter depth below the seafloor. Together with isotopic evidence, the pore fluid chemistry indicates microbial sulfate reduction utilizing the hydrothermal methane. The *Calyptogen* colony would be supported by the product hydrogen sulfide. This idea is supported by a result of microbial population analysis based on taxonomic grouping of gene clone sequencing, which detected sulfate reducing bacteria and methane oxidizing archaea in the sediment sample.

## Contrast compositions of minerals, kerogens and lipid-biomarkers in 1.9 Ga shallow- and deep-water sedimentary rocks of the Gunflint Formation, Canada

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In order to constrain the microbial ecosystem of Paleoproterozoic oceanic environments, geochemical analyses were performed on the ca. 1.9 Ga Gunflint Formation, Canada. The examined samples are divided in shallow- and deep-water sequences based on their lithologies and field observations. Hematitic oolites were the representative lithology for the shallow-water sequence and the deep-water sequences contain sideritic banded iron formation. Such contrast in Fe-bearing minerals in chemical sediments suggests the stratified oxic-anoxic oceans during deposition of the Gunflint Formation.

The high productivity of microbes at around the shallow- and deep-water sequences is suggested by the local occurrence of phosphorites. As-rich framboidal-like pyrite was found with euhedral pyrite around such phosphorites, suggesting that sulfate-reducers were active both in anoxic parts of ocean waters and also in sediments.

Kerogens were extracted from 50 samples. Their stable carbon isotope compositions were ranging from -33.6 ‰ to -31.4 ‰ (PDB). 2- $\alpha$  methyl hopane were identified by GC-MS analyses of lipid-biomarker extracted from black shale samples. These results suggest that cyanobacteria were the major primary producers to support the ecosystem both in oxic and anoxic parts of Gunflint oceans. H/C ratios of kerogens were identical in all samples, although shallow-water kerogens were more enriched in N, implying the different nitrogen-fixation pathway between the shallow- and deep-water ecosystem.

## Comet 81P/Wild 2 dust versus cometary interplanetary dust

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Samples returned by the Stardust mission from Comet 81P/Wild 2, believed to originate in the Kuiper Belt, were expected to include materials found in chondritic porous interplanetary dust particles (CP IDPs), collected in the stratosphere, since much of this latter dust population derives from cometary bodies. Some CP IDPs are highly enriched in presolar grains, isotopically anomalous grains inherited from the interstellar medium and presolar molecular cloud, and Wild 2 was anticipated as a reservoir of presolar material. A search in Stardust samples for the most recognizable and most abundant silicate materials in CP IDPs has, to date, turned up empty-handed [1]. A single enstatite whisker (readily identifiable in CP IDPs) is reported in the returned Wild 2 sample but with crystallographic orientation inconsistent with those in CP IDPs. Objects like GEMS (which are abundant in CP IDPs and include verified presolar amorphous silicates) are found in abundance in the returned sample; however, we have demonstrated their creation on capture by impact of pyrrhotite into silica aerogel at Stardust speeds.

The lack of enstatite whiskers and recognizable GEMS, combined with existing evidence of characteristic inner solar system refractory materials, low D/H ratios, and a dearth of presolar grains and refractory carbon, indicate indigenous outer nebula material is probably rare in 81P/Wild 2. Instead, the returned sample resembles materials in chondritic meteorites re-emphasizing the petrogenetic continuum between comets and asteroids and raising questions concerning early solar system transport and small solar system body classification. CP IDPs remain an invaluable source of cosmically primitive material.

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## Integrated thermal history analysis of the Beaufort-Mackenzie basin using multi-kinetic apatite fission track thermochronology

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Sixty apatite fission track (FT) samples (mainly cores from Cenozoic, Cretaceous and Devonian rocks) were collected from twenty-five petroleum exploration wells distributed across the Beaufort-Mackenzie Basin (BMB), northern Canada, as part of an integrated study of petroleum systems. In addition, vitrinite reflectance and shale compaction data were obtained to help constrain maximum paleotemperatures and erosion magnitudes. Sample apatite grains are heterogeneous in composition and yield mixed FT age populations. Older age grains have elevated concentrations of elements (e.g. Fe, Mg, Mn, Cl) that make them more FT retentive (higher annealing temperature) than typical fluorapatite. Elemental data were used to calculate  $r_{m0}$  values [1] corresponding to apatite populations with different FT annealing kinetics. FT age populations determined using the  $r_{m0}$  parameter show good agreement with those derived using the binomial peak-fitting program, BINOMFIT [2]. In general, the  $r_{m0}$  parameter produced more consistent and better defined kinetic populations than other commonly used parameters (e.g. Cl content, FT etch figure size).

Thermal histories were obtained for the FT samples using an inverse Monte Carlo model [3] incorporating the multi-kinetic FT annealing scheme of Ketcham *et al.* [1] that treats each kinetic population in a sample as a separate thermochronometer, thus enhancing thermal history resolution. Model solutions are consistent with observed FT age and length parameters and conform to other geological constraints (present temperature, thermal maturity, rate bounds from preserved stratigraphy). The multi-kinetic FT samples constrain both the post-depositional heating and cooling histories of the Cretaceous-Cenozoic sedimentary successions comprising the BMB as well as the cooling histories of the exhumed source areas from which these sediments were derived.

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## What does cause a bell-shaped profile of aqueous As in contaminated Holocene aquifer?

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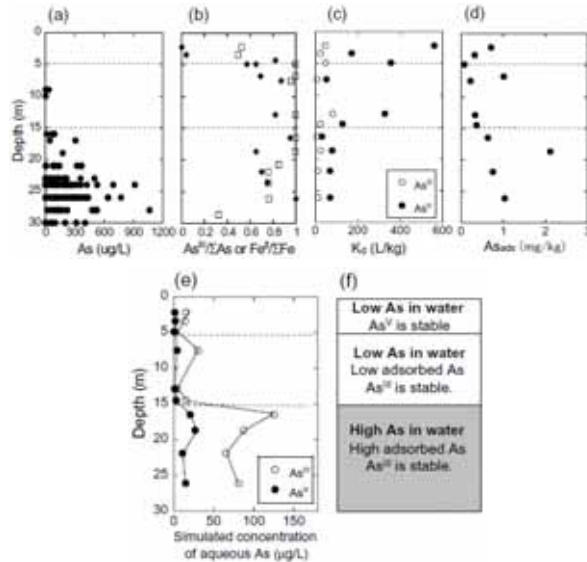
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Groundwater in Bangladesh is seriously contaminated by As, and aqueous As typically distributes as a “bell-shape” profile. (Fig. 1a) [1]. Interestingly, this profile is not consistent with changes in oxidation states of As and Fe, which are the key factor to control mobility of As (Fig. 1b) [2]. We investigated sediment-water As-partitioning to reveal formation processes of the bell-shaped profile.

Apparent distribution coefficient ( $K_d = A_{s,ads}/A_{s,aq}$ ) is always higher for  $As^V$  than  $As^{III}$  (Fig. 1c). Small variation of  $K_d(As^{III})$  is not consistent with the bell-shaped profile. However, simulated concentration of dissolved As ( $A_{s,ads} * K_d^{-1}$ ) well corresponds the bell-shaped profile due to significantly lower concentration of P-extractable As from 4 to 15 m than below 15 m (Fig. 1 d,e). Hence, fundamental difference between two depth regions with high and low As abundance is amount of adsorbed As. The findings of this study are summarized in Fig. 1f.



**Figure 1:** Depth profiles of (a) dissolved As, (b) oxidation states of As and Fe in sediment, (c)  $K_d$  of  $As^{III}$  and  $As^V$ , (d) P-extractable As, (e) simulated concentration of aqueous As, and (f) schematic figure of formation processes of bell-shaped profile.

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## Some geochemical consequences of the dynamics and melting of a veined mantle

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The processes that deliver chemical heterogeneity from the mantle source to melts erupted at the surface constitute a vibrant topic in geodynamics and igneous geochemistry. Our chemical-geodynamic models couple upper mantle flow and temperature to melting of distinct source components, which have melting functions that depend on volatile content and mafic versus ultramafic composition. Models predict that the isotopic and incompatible element compositions of eruptible magmas are sensitive to vertical variations in mantle upwelling as well as lithospheric thickness. One finding is that many of the major differences in Sr, Nd, Pb, and He isotopic characteristics of hotspot basalts, compared to non-hotspot, mid-ocean ridge basalts, can be caused by relatively thick lithosphere and buoyant mantle upwelling beneath hotspots, which both tend to preferentially melt the least refractory components. The broader implication is that any mantle-wide compositional stratification is weaker than previously thought. Another finding is that the upper mantle dynamics associated with mantle plume-lithosphere interaction can give rise to a regional spatial zoning in surface lava composition if the source is veined but, itself, lacks any regional-scale compositional zoning. For an intra-plate hotspot such as Hawaii, these models predict some of the major differences between the “Loa” and “Kea” sub-chains as well as between the main shield-building phase, the post-shield phase, and secondary (including rejuvenated) volcanism in terms of Nd-isotopes. These results pave the way for future work to better constrain the nature of any potential zonations in the mantle. Finally, a simplifying assumption of the above models is that the flux of melt from each source component is proportional to the rate that each melts by decompression, without being influenced by chemical reactions with other components. The degree to which chemical reactions affect lava compositions depends on whether the upward migration of melts from individual heterogeneities occurs by pervasive percolation over large volumes of the mantle, or is confined to high-porosity channels that remain physically separate from most of the surrounding mantle.

## Heavy metal concentration of river sediment in the light of the environmental quality standard value at the Kiso and Syounai Rivers in Nagoya, Japan

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The river sediment is basically composed of clastic materials derived from the surface of the Earth. The purpose of our study is to clarify the quantitative estimation of ratio of influence given to river sediment of nature and human activity by using of heavy metals [1-4].

We show the geochemical and geological characteristics of stream sediments from the Kiso and Syounai Rivers that flow in Nagoya, Japan.

We show research results of the degree of contamination in Shounai River that is the one of the most polluted river in Japan. It also searched for Kiso River in the same Noubi Plain for the comparison. Sediment samples collected from various points along the upper and lower streams were subjected to content analysis and elution analysis (using liquate (flow) out test) on the heavy metals like Cd, CN, Pb, Cr, As, Hg, Ni, Zn and Cu from the river sediment for the purpose of environment assessment.

In Kiso River, slightly high content value of As (234ppm) by the past old metal mine was detected in the middle stream. But the lower stream was diluted by self cleaning power of the river. In Syounai River, Pb, Cr, As, and Hg are relatively high content in the mouth region. Particularly, the value of elution of As slightly exceeded the environmental standard value.

This study is the first research that investigated sediment of those rivers in the light of the environmental quality standard in Nagoya area, Japan.

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## Holocene record of decadal variability from the NE Pacific

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A 40 m long marine sediment core raised from Effingham Inlet, an anoxic fjord on the west coast of Vancouver Island, Canada, yields a high-resolution record of Holocene climate variability. Forty-six <sup>14</sup>C AMS dates comprise the age model and downcore sampling provides a record with 5 cm (20 yr) and 1.5 cm (7 yr) resolution. Spectral analysis of % opal, a proxy for diatom productivity, identifies the 20 and 50-year periods of the PDO/NPI. Both periods are present to some degree in the Early Holocene, while only the 50-year period is evident in the late Holocene. These data imply that PDO "regime shifts" would have been more frequent in the Early Holocene relative to the last few thousand years. Coherence analysis between the Effingham Inlet data and Jellybean Lake  $\delta^{18}\text{O}$  records (SW Yukon)[1] indicate regional coherence at periods of 45, 70, 360 and 510 years between productivity in Effingham Inlet and changes in the Aleutian Low strength. The significant coherence between these two sites at the ~50 year period strongly implies that variability in the strength of the Aleutian Low has driven a broad climatic teleconnection from Vancouver Island to Alaska over the entire Holocene.

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## The paradoxical trend of $\delta^{13}\text{C}_{\text{org}}$

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A well known trend manifesting by the  $\delta^{13}\text{C}_{\text{org}}$  towards a heaviness, from ancient sediments to the young ones, has been undoubtedly found long ago being studied on numerous occasions in a lot of geochemical works devoted to the geological time lasting development of the biosphere. Based on the geochemical processes regularities, possible mechanisms of this phenomenon origin were proposed to explain a nature of the global carbon isotope composition variations in biosphere [1, 2].

The situation paradox deals with a fact that due to a several isotope effects processed inside the living organisms, the isotopic-light carbon form is to be predominantly assimilated as compared to the heavier one. This is what a biological isotope effect is all about. The geochemical paradox mentioned is that it would be far more logical to expect the reverse effect in the observing trend which, nonetheless, is not the case.

In a present work, an additional and a very peculiar mechanism suitable to involve the  $^{13}\text{C}$  isotope into the Earth bioorganic reservoir has been offered to legitimize the observing trend vector.

The key point of this mechanism consists in a crucial need for  $^{13}\text{C}$  participation in the isotopy DNA-conformational effect which was presumably taking part in the life systems molecular evolution starting from its very beginning [3-4].

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## Thermal and flow structure of subduction zones and water transportation into the deep mantle

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Processes in subduction zones are key to understanding many of the geological phenomena unique to the Earth: e.g., earthquakes, arc magmatism, regional metamorphism, orogeny, continental growth, as well as global budgets and transportation of material and energy, bridging the surface environment and the Earth's interior. Thermal and flow structure of the subducting slab and the overlying mantle wedge is one of the most important factors that govern the various processes mentioned above, yet it remains to be constrained. In this paper, in order to better constrain the thermal and flow structure of subduction zones, geological and seismological observations and the corresponding numerical modeling are presented and consolidated. In subduction zones, thermal structure, flow structure and water distribution interplay, and they need to be solved consistently. Consequently, the numerical modeling includes generation and migration of aqueous fluid, and its reaction with the convecting solid. The model results show that an aqueous fluid released from the subducting oceanic crust forms a serpentinite layer in the mantle wedge just above the subducting slab. This layer acts as a lubricant between the subducting slab and the overlying mantle wedge, and greatly affects the thermal and flow structure to contribute to water transportation to the deep mantle. Recent seismic studies support existence of such a hydrous layer just above the subducting slab<sup>1</sup>. Even after the completion of dehydration of major hydrous mineral phases in the subducting materials, especially at the base of the mantle wedge just above the subducting slab, nominally anhydrous phases can carry a significant amount of  $\text{H}_2\text{O}$  ( $1.1$  to  $7.8 \times 10^{11}$  kg yr<sup>-1</sup>) into the deep mantle<sup>2</sup>. This water and the associated components may be accumulated in the deep mantle to develop unique isotopic character reflecting aqueous fluid-rock reaction, and could be the source of one of the two independent components that have recently been found in the isotopic compositional space of oceanic basalts<sup>3</sup>.

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## Chromium mobilization from the unsaturated zone

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Recent work has shown that natural Cr(VI) concentrations in oxic, alkaline aquifers, especially those in mafic terrains, occasionally exceed the California Maximum Contaminant Level for chromium of 50 µg/L.  $\delta^{53}\text{Cr}$  data in the western Mojave Desert intended to define the margin of a chromium contamination plume in an area having high natural background Cr(VI) concentrations revealed high Cr(VI) concentrations having near-zero  $\delta^{53}\text{Cr}$  compositions at the top of the water table upgradient from obvious point sources of contamination. These values may be related to overlying land uses, especially land uses associated with large concentrations of animals. In the study area, high-sulphate concentrations, exceeding 2,000 mg/L, that are associated with animal-waste discharges appear to have mobilized Cr(VI) sorbed on iron and manganese oxides. This may occur because sulphate is an oxyanion having sorptive properties similar to those of Cr(VI). Oxic conditions in the unsaturated zone limit the reduction of Cr(VI) to Cr(III) despite the obvious presence of organic reductants. The reduction of Cr(VI) to Cr(III) is further limited by high-nitrate concentrations, exceeding 200 mg/L as N, that provide a more thermodynamically favourable electron donor—thereby partly inhibiting the reduction of Cr(VI) to Cr(III). As long as high-nitrate concentrations persist, Cr(VI) can persist in both the unsaturated and saturated zones at the site, even if anoxic conditions develop. Although these processes are probably more important in unsaturated zones in mafic terrains they also may occur in other geologic settings.

## Evolution of deglacial North Pacific abyssal circulation based on $\Delta^{14}\text{C}$ , $\delta^{13}\text{C}_{\text{benthic}}$ and $^{231}\text{Pa}/^{230}\text{Th}$

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Recent  $\Delta^{14}\text{C}$  results from the Gulf of Alaska clearly show that the deep North Pacific was more poorly ventilated during the LGM when compared to today and that ventilation improved during the last glacial termination. During the last deglaciation, export production increased dramatically *ca.* 14.5 – 15 kybp across the entire subarctic Pacific, while the oxygenation of bottom waters increased as indicated by a decrease in redox-sensitive trace metal accumulation in the sediments. The remarkable temporal coincidence of changes in the deep and surface oceans suggests that the arrival of better-oxygenated deep waters was mechanistically linked to an increase in the upward flux of nutrients to the surface thus fuelling primary productivity. The close coincidence of this with the start of the Bolling warm period in the North Atlantic hints that a tight physical relationship linked the North Pacific circulation and the reinvigoration of the Atlantic meridional overturning at this time.

On the other hand, sedimentary  $^{231}\text{Pa}/^{230}\text{Th}$  measured at ODP sites 882 (Emperor Seamount region) & 887 (Gulf of Alaska) show a sustained, parallel increase starting at around 17.5 kyr – significantly before any regional increase in particle flux. This signal is tentatively interpreted as illustrating the dissipation of a large  $^{231}\text{Pa}$  pool accumulated in a relatively stagnant glacial abyssal Pacific Ocean at the onset of deglaciation.

In this contribution we will test the applicability of  $^{231}\text{Pa}/^{230}\text{Th}$  as a proxy for relative changes in deep Pacific circulation across the last glacial termination. In addition, the apparent timing discrepancy between  $\Delta^{14}\text{C}$  and  $^{231}\text{Pa}/^{230}\text{Th}$  and its potential implication for the carbon cycle will be discussed.