

Smoke source strength from satellite measurements of fire strength

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Chemical transport models currently derive their smoke emission sources from counts of fire hot spots detected from satellites, usually with single daily overpasses. However, fires vary in size and strength, with prominent diurnal cycles that vary from one biome to another, making the use of pixel counts measured at the same time of day very unreliable for estimating smoke sources. Fortunately, the Moderate-resolution Imaging Spectro-radiometer (MODIS) twin sensors onboard the Terra and Aqua satellites, not only detect fires everywhere at four strategic times of day, but also measure their strength in the form of fire radiative power (FRP) or rate of release of fire radiative energy (FRE). FRP is now also being derived from the Spinning Enhanced Visible and Infrared Imager (SEVIRI) sensor onboard the geostationary Meteosat-8 platform, which observes Africa and Europe virtually every 15 mins. The SEVIRI measurements show that MODIS 4-times-a-day measurements capture the essence of the fire diurnal cycle. Therefore, MODIS is currently the only satellite data source ideal for estimating daily smoke emissions globally. Although MODIS has been in operation since the last 9 years, regrettably, this rare but formidable data resource it provides (FRP) has remained largely underutilized. However, in a number of recent studies, FRP has been found to be directly proportional to both the rate of biomass consumption and the rate of smoke aerosol emission. Indeed, a FRE-based emission coefficient (Ce), which is a simple coefficient to convert FRP (or FRE) to smoke aerosol emissions was derived for different parts of the world. The results obtained from satellite have been reproduced in the laboratory, and the ingestion of FRP in models is now being tested using the Goddard Chemistry Aerosol Radiation and Transport (GOCART) model. In this presentation, we will show the preliminary results of using FRP to improve the smoke emission source characterization and impacts analysis.

Two-stage growth evolution of hydrothermal quartz: Impurities quantify the story

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Large-scale hydrothermal fluid systems control the thermal evolution of the Earth's crust. Quartz crystals, the primary product of circulating aqueous fluids, contain fluid inclusions and chemical impurities that document their growth history in hydrous environments [1, 2]. High-resolution FTIR measurements show that natural quartz crystals are composed of sector zones characterized by distinct concentrations of hydrous impurities. Some hydrothermal environments (e.g., Minas Geras, Brazil) produce crystals that document a single phase of growth characterized by growth on only the six terminal rhombohedral faces [1]. Here, we document the distribution of defect abundances in several crystals extracted from a single vug from Le Chang City, Guangdong Province, China that record two distinct phases of growth. Each crystal contains: (1) an inner core, with elevated AlOH concentrations (50-200 ppm), intermediate LiOH and HOH concentrations (10-100 ppm) and negligible KOH concentrations (< 5 ppm); and (2) a thick outer rim with LiOH and HOH > AlOH, and KOH > 5 ppm. Rim thickness remains constant up the length of the crystal, and 'concentric' twin bands indicate that this second stage of growth served to 'coat' the pre-existing core on both terminal & *m* prism faces.

The distributions of hydrous impurities in quartz provide additional insights into their host hydrothermal systems. Variations in the relative abundance of different chemical species provide insights into changing fluid chemistry, and diffusion profiles observed near crystal edges document thermal events after their growth. We use ion probe analyses to identify individual IR absorption bands and show that the Guangdong crystals document an evolving host fluid chemistry. Their cores show classic diffusion profiles toward the contact with the rims, and suggest the cores had fully grown before the AlOH-poor coating was added onto their respective *m* faces. This phenomenon appears to have impacted all of the crystals within the same vug.

[1] Ihinger and Zink (2000) *Nature*, **404**, 865-869. [2] Jourdan et al. (2009) *Eur. J. Mineral.*, **21**, 219-231.

Sensitivity of glacier and climate reconstructions in high mountain regions to uncertainties of ^{10}Be surface exposure dating

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Reliable Late Quaternary glacier and climate reconstructions have long been challenging particularly in semi-arid high mountain regions, where organic material for radiocarbon dating is scarce. Surface exposure dating of glacial deposits using terrestrial cosmogenic nuclides, like ^{10}Be , may enable establishing glacial chronologies more precisely, but geological and systematic methodological uncertainties need to be addressed. Here we compare 'virtual' exposure ages on global grids and along longitudinal transects in order to illustrate that systematic uncertainties due to the choice of the scaling system can result in age discrepancies more than 20%, depending on geographic location and exposure time. Particularly at high elevations in the subtropics and mid latitudes this prevents drawing paleoclimatic conclusions on millennial timescales. Provided that the recent developments in scaling are appropriate, our case study from the Central Andes illustrates that the local Last Glacial Maximum in the tropical Andes occurred at ~ 25 ka - roughly in-phase with the global LGM - and not at ~ 30 ka as inferred previously. Systematic uncertainties decrease further south, increasing confidence in interpreting Lateglacial moraines (16-13 ka) from ~ 15 - 30°S as evidence for an intensification of the tropical circulation, and pre-LGM moraines (~ 35 ka) from 30 - 40°S as evidence for stronger or more northerly westerlies. Our second case study from the Pamir Mountains shows that environments with long-lasting landscape instability are prone to geological uncertainties, which cause large scatter in exposure ages. Applying the 'oldest age model', we conclude that (i) the maximum glaciation at our study site near Lake Yashilkul occurred during MIS 4, (ii) glaciers were less extensive during MIS 2, likely due to increasing aridity over the course of the last glacial cycle, and (iii) an intensified monsoonal circulation was probably responsible for moraines being deposited during MIS 3.

Deposition of volatiles from Erebus volcano in Antarctic snow and ice

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The persistently degassing Erebus volcano (Ross Island, Antarctica) has a significant influence on the regional atmospheric and cryospheric chemistry. Its rare magma composition combines with ambient atmospheric conditions to produce unusual emissions released from the surface of its lava lake. We report analyses of volcanic deposition from Erebus collected during consecutive Antarctic field seasons (2005-2007). The deposits included: (i) snow from areas believed to be contaminated by the volcanic plume, (ii) snow containing ash; (iii) 'yellow ice' which are distinctive ice deposits of bright-yellow colour. All the plume-affected deposits have highly elevated concentrations of chloride and fluoride (≥ 1000 ppm), sulphate (≥ 240 ppm) and an array of metal cations (Al, Na, K, Fe, S, Ca, Mg and Pb being the most abundant). Abundances of Na, K and Al correlate strongly with those of halides; consistent with the known composition of aerosol particles emitted by Erebus. Yellow ice showed higher ionic concentrations than the snow. Ash-snow had elevated concentrations of selected ions (F, Cl, and certain metals), believed to be caused by hydrolysis of silicate minerals. Halide/sulphate molar ratios in the deposits are over an order of magnitude higher than in the gas phase. Dry deposition and/or snow scavenging of halide species is much more efficient than that of SO_2 and sulphate. The relative proportions of metals in the snow/ice were compared with those in the airborne plume to show that the lighter metals (Na, K, Mg, Ca, Fe) tend to be more enriched in the snow than heavy metals (Cr, Ni, Cu, Cd and In). It is proposed that the low ambient atmospheric temperature has a 'cold trap' effect causing selected ions to resist deposition.

Pressure dependence of partition coefficients between olivine and peridotite melt

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In order to understand the crystallization process of global magma ocean, precise knowledge on the element partitioning at various pressures is essentially important. We have determined PC-IR (partition coefficient, ionic radius) diagram for 32 elements between olivine and peridotite melt at 2, 5, 10, and 14 GPa. Two types of starting materials were prepared from a fertile peridotite KLB-1 [1] with different levels of trace elements. High-pressure melting experiments were performed using a piston-cylinder apparatus and a multi-anvil apparatus at the Magma Factory, Tokyo Inst. of Technology. Chemical analyses were performed using EPMA (JEOL-8800) for major and minor elements and LA-ICP-MS for trace elements (ArF excimer laser and a quadrupole mass spectrometer, 30 µm laser beam, NIST610 glass standard). Partition coefficients were calculated and were plotted on the PC-IR diagram. The results of this study are in general agreement with previous studies on similar compositions (analysis by EPMA [2]; by SIMS [3]) except that the shape of the peaks and pattern of the parabolas were tightly constrained in the present study. PC-IR diagram for trivalent cations between olivine and peridotite melt was tightly constrained for the first time with 14 elements (including 8 REE). The partition coefficient for Al increases with pressure ($D_{Al}=0.012$ at 2 GPa, 0.048 at 14 GPa) while that for all other trivalent cations decreases with increasing pressure (e.g., $D_Y=0.0077$ at 2 GPa, 0.0019 at 14 GPa). The pressure effect on the PC-IR diagram cannot be explained simply by the lattice strain model [4] but requires some additional factors. Increase in D_{Al} may be explained by the combination of two types of substitutions ($Mg^{2+}, Mg^{2+} \leftrightarrow (Na^+, Al^{3+})$ and $(Si^{4+}, Mg^{2+}) \leftrightarrow (Al^{3+}, Al^{3+})$). Decrease in D values for other trivalent cations implies that the latter type of substitution is the dominant mechanism.

[1] Takahashi (1986) *J. Geophys. Res.* **91**, 9367-9382. [2] Suzuki and Akaogi (1995) *Phys. Chem. Minerals* **22**, 411-418. [3] Taura *et al.* (1998) *Phys. Chem. Minerals* **25**, 469-484. [4] Blundy and Wood (1994) *Nature* **372**, 452-454.

Tethys-wide occurrence of Lower Aptian *Lithocodium-Bacinella* facies: Shoalwater expression of basinal OAE1a black shales

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Lithocodium aggregatum and *Bacinella irregularis* are now extinct microencrusters of unknown taxonomic origin that thrived in (sub)tropical platform environments. During parts of the Early Aptian, these organisms experienced bloom periods and temporarily replaced rudist-coral assemblages as the dominant framework builders. Within the limitations of geological time resolution, this “out-of-balance” shoalwater facies seems to be coeval with the OAE1a-related black shale deposition in oceanic basins but the triggering environmental factors that caused this mass occurrence remain insufficiently understood. Having previously established the OAE1a-synchronous nature of *Lithocodium-Bacinella* facies across the Arabian Platform in Oman [1], recent work focuses on OAE1a time-equivalent exposures in Croatia, France and Portugal. Time correlation is based on high-resolution carbon-isotope stratigraphy supported by Sr-isotope stratigraphy focussing on selected rudist shell material. It is not the mere presence of *Lithocodium-Bacinella* as such that is of interest here – *Lithocodium-Bacinella* co-existed with many other neritic organisms throughout much of the Mesozoic – but the transient mass occurrence of these microencrusters and the coeval demise of the dominant mid-Cretaceous framework-builders (rudists and corals). Obviously, the transient dominance of *Lithocodium-Bacinella* facies is but one of the known responses of neritic platform systems to factors that also caused OAE1a. From other Tethyan localities, platform drowning [2] or the presence of bituminous limestones [3] have been reported. An improved comprehension of the effects of C-cycle perturbation on neritic palaeo-ecosystems is instrumental in understanding anoxic events to their full extent.

[1] Immenhauser *et al.* (2005) *Sedimentology* **52**, 77-99. [2] Weissert *et al.* (1998). *Palaeogeography, Palaeoclimatology, Palaeoecology* **137**, 189-203. [3] Heldt *et al.* (2008) *Palaeogeography Palaeoclimatology Palaeoecology* **261**, 246-260.

Fractionation of iron isotopes during estuarine mixing in Ob, Yenisey and Lena freshwater plumes

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Iron isotopes were measured in suspended matter (>0.2 µm) in the Ob, Yenisey and Lena River freshwater plumes during the International Siberian Shelf Study 2008 (ISSS-08). The $\delta^{56}\text{Fe}$ value was around zero within the Lena River and close to the river mouth, but changed to more negative values in the outer parts of the plume. In both the Ob and Yenisey plumes suspended matter in the surface water had clearly negative values whereas samples close to the bottom showed values close to zero.

It has previously been suggested that total Fe in river suspended matter (>0.2µm) in boreal regions is roughly a mixture of three phases, detrital particles ($\delta^{56}\text{Fe}$ around zero), oxyhydroxide particles ($\delta^{56}\text{Fe}$ positive) and C-Fe particles ($\delta^{56}\text{Fe}$ negative). We suggest that the $\delta^{56}\text{Fe}$ pattern observed in this study is the result of relatively rapid removal of detrital particles and Fe-oxyhydroxides, leaving a suspended fraction with negative values in the surface water in the outer parts of the freshwater plumes. Hence, during estuarine mixing of suspended particles heavy iron isotopes are deposited close to the river mouth, whereas light isotopes are exported to open ocean water.

Nitrogen isotopes in volcanic fluids of different geodynamic settings

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Nitrogen isotopes, $\text{N}_2/^{36}\text{Ar}$ and $^3\text{He}/^4\text{He}$ were measured in volcanic fluids within different geodynamic settings. Subduction zones are represented by Aeolian archipelago, Mexican volcanic belt and Hellenic arc, spreading zones – by Socorro island in Mexico and Iceland and hot spots by Iceland and Islands of Cabo Verde. The $\delta^{15}\text{N}$ values, corrected for air contamination of volcanic fluids, discharged from Vulcano Island (Italy), highlighted the presence of heavy nitrogen (around $+4.3 \pm 0.5\%$). Similar $\delta^{15}\text{N}$ values (around $+5\%$), have been measured for the fluids collected in the Jalisco Block, that is a geologically and tectonically complex forearc zone of the northwestern Mexico [1]. Positive values ($\delta^{15}\text{N}$ around $+3\%$) have been also measured in the volcanic fluids discharged from Nysiros island located in the Hellenic Arc characterized by subduction processes. All uncorrected data for the Socorro island are in the range of -1 to -2% . The results of raw nitrogen isotope data of Iceland samples reveal more negative isotope composition (about -4.4%). On the basis of the non-atmospheric N_2 fraction (around 50%) the corrected data of $\delta^{15}\text{N}$ for Iceland are around -16% , very close to the values proposed by [2]. In a volcanic gas sample from Fogo volcano (Cabo Verde islands) we found a very negative value: -9.9% and -15% for raw and corrected values, respectively.

[1] Inguaggiato *et al.*, (2004) *G³*, **5**, Q12003. [2] Mohapatra *et al.* (2004) *G³*, **5**, Q01001.

Assessment of increased CO₂ on growth and variation of trace elements of coral polyp skeletons (Genus *Acropora*)

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Ocean acidification caused by increased atmospheric CO₂ is feasible threat for calcifying organisms including corals. Decalcification by lower pH has been reported in several marine organisms, such as foraminifera, sea urchin and corals. In order to evaluate the impact of lower pH on calcifying organisms, the range of tolerable pH on their various life stages should be investigated. In addition, study on variation of chemical compositions in calcifying organisms against pH is important to understand the mechanism of biomineralization for each organism.

In this study, we assessed the effects of increased CO₂ on early life stages of scleractinian corals (*Acropora* spp.), which is one of the most dominant species around Okinawa Island, Japan. In this experiment, four steps of pH (SWS) were controlled using filtered seawater which was bubbled by pure CO₂ at 27 °C (pH 6.6, 7.3, 7.6 and 8.0). Approximately 40 coral polyps were cultured more than 10 days under each pH setting and several polyp skeletons were weighted one by one using a microbalance. Then trace elements (Mg/Ca, Sr/Ca, Ba/Ca and U/Ca) in polyp samples were measured by ICP-MS (HP4500). As a result, smaller polyps were found at lower pH, indicating a positive relation between polyp growth and pH. However, even at pH 7.3, which is under-saturation for aragonite, skeletons were not dissolved and/or grown slightly. It is suggested that a specific physiochemical mechanism may control pH in the coral. Furthermore, as previous studies suggested, Mg/Ca in coral skeletons seem to be controlled by coral growth and it could play important role on coral biomineralization.

Metasomatism in the mantle wedge beneath the Avacha volcano, Kamchatka from xenolith data

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Mantle wedge rocks are believed to have experienced metasomatism by fluids expelled from subducted oceanic lithosphere. Many aspects of this phenomenon continue to be debated and can be addressed by studies of rare peridotite xenoliths hosted by subduction-related volcanic rocks.

Petrographic, major and trace element data were obtained on 17 large and fresh harzburgites and a smaller number of veined xenoliths from the active andesitic Avacha volcano in southern Kamchatka peninsula, Russia (see also [1]). A distinctive characteristic of the Avacha harzburgites is a combination of variable but generally high modal opx (18-30%) with very low modal cpx (1.5-3%). At a given olivine (or MgO) content, they have higher opx (and SiO₂) contents, and lower cpx (as well as Al₂O₃ and CaO) contents than normal refractory peridotite xenoliths in continental basalts; the Mg-Si and Al-Si trends resemble those in cratonic peridotites. These features may indicate either fluid fluxing during melting in the mantle wedge or selective metasomatic enrichments in SiO₂ to transform some olivine to opx. The latter is consistent with replacement of olivine by coarse opx seen in some xenoliths. Whole-rock enrichments in silica in the Avacha suite are restricted to samples with abundant coarse opx and are not correlated with the amounts of fine-grained, late-stage re-crystallisation products, which mainly replace coarse opx and contain euhedral olivine and amphibole. This is at odds with earlier work [2] that argued that the fine-grained opx record a major metasomatic event responsible for the enrichment of the mantle wedge in silica.

Two types of veins are identified in the Avacha xenoliths. Coarse opx-rich veins may have formed in the ancient event that produced silica enrichments in the harzburgites. Thin, fine-grained, cross-cutting veins consist of subhedral opx with variable olivine, cpx, amphibole, glass and accessory sulfides. These veins formed shortly before the transport of the xenoliths to the surface. Trace element patterns of their minerals are commonly different from those in whole-rock harzburgite xenoliths suggesting multiple sources of parental fluids including those linked to subducted oceanic crust.

[1] Bénard and Ionov (2009) *GCA*, this volume. [2] Ishimaru et al. (2007) *J. Petrol.* **48**, 395-433.

Biomineralisation of nano-Fe(III) phases in inland waterways

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Discharge of Fe(II)-rich groundwaters to surface-waters results in biomineralisation and the formation of Fe(III)-mineral accumulations in inland waterways. This study describes their micromorphology, pore-water chemistry and environmental occurrence in a Tertiary floodplain setting.

Fe(III) precipitates were pH 6.2-7.2, sub-oxic (Eh 59-453 mV), with dissolved Fe(II) ranging from 0.1 to 81.6 mg L⁻¹. X-ray diffraction indicated a dominance of 2-line ferrihydrite, with lesser amounts of goethite and lepidocrocite. Electron microscopy revealed the nano-crystalline properties of the 2-line ferrihydrite (Fe₅HO₃·4H₂O), goethite (α-FeOOH) and lepidocrocite (γ-FeOOH). Overall, the results demonstrated distinct variations in Fe(III) mineralogy and micromorphological characteristics. Preliminary groundwater oxidation data found the importance of *Leptothrix ochracea* in promoting the precipitation and stabilisation of these nano-particulate Fe(III) minerals. This biomineralisation resulted in abundant sheath and aggregate microstructures of predominantly 2-line ferrihydrite (Fig 1a), and some lepidocrocite crystals (Fig 1b). The implications to water quality of this biomineralisation process are explored.

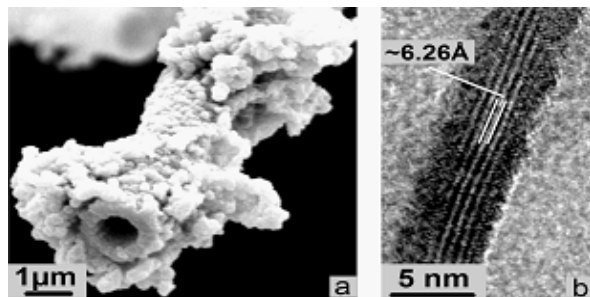


Figure 1 a) *L. ochracea* sheath and nano-particulate ferrihydrite aggregates; b) lepidocrocite nano-crystal ~5 atomic layers thick perpendicular to the (020) lattice plane (d-spacing = ~6.26)

Fluid geochemistry of the Suiyo hydrothermal field at the Izu-Bonin arc submarine volcano

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We revisited the Suiyo hydrothermal field (28°34'N, 140°30'E, depth=1360m) during NT07-08 dive missions conducted using ROV *Hyper Dolphine* (Japan Agency for Marine Science and Technology). We confirmed that both temperature (T = 300 degC) and chemistry of the venting hydrothermal fluids have been stable since the first discovery in 1992, which suggests equilibrium of hydrothermal interactions within the aquifer. Rare Earth Element pattern in the hydrothermal fluids showed Light REE enrichment with a positive Eu anomaly.

Shallow drilling using BMS (Benthic Multi-coring System) revealed hydrothermal alteration of pyroclastic rocks of dacite-rhyolite compositions beneath the area of active venting [1]. Enrichment in CO₂ of the venting fluid [2] could be responsible for intense hydrothermal alteration. As hydrothermal clay minerals, montmorillonite, chlorite and mica were identified. Chemical composition of the altered core samples showed uptake of potassium, which may be responsible for high calcium concentration rather than potassium of the hydrothermal fluid.

[1] Marumo K. *et al.* (2008) *Resource Geology*, 58, 220-248.

[2] Toki T. *et al.* (2008) *J. Geophys. Res.*, 113, B08S13

Geochemistry of 1.9 Ga gunflint formation in Canada: Unique oceanic environments and microbial activities

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Geochemical analyses were performed on the ca. 1.9 Ga Gunflint Formation, Canada in order to constrain the microbial ecosystem of Paleoproterozoic oceanic environments. The examined samples are divided in shallow- and deep-water sequences based on their lithologies. Hematitic oolites were the representative lithology for the shallow-water sequence and the deep-water sequences contain sideritic banded iron formation. Such contrast in water depth is corresponded to stratified oxic-anoxic ocean situation deposition of the Gunflint Formation.

Kerogens were extracted from 50 samples. Their stable carbon isotope compositions were ranging from -33.6 to -25.1 ‰ (PDB). 2 α -methyl hopane were identified by GC-MS analyses of lipid-biomarker. These results suggest that cyanobacteria were the major primary producers to support the ecosystem both in oxic and anoxic parts of the Gunflint ocean. The productivity of cyanobacteria was extremely high forming thick microbial mats on the shallow part of oceans. Intensive carbon recycling was occurring in such mats, supporting anaerobic life, including methanogens.

S(pyr)/C(org) ratios of examined samples were higher than the results of previous studies. The stable sulfur isotope compositions of pyrites were range from -1.1 to +26.9 ‰ (CDT). These results indicate that ca. 1.9 Ga Gunflint ocean was sulfate-rich ocean, promising high activity of sulfate reducers in particular thick microbial mats in the shallow part of the Gunflint ocean.

H/C and N/C atomic ratios of kerogens were distinctive between oxic and anoxic conditions. As a result, oxic-water dominant kerogens were more enriched in nitrogen than anoxic-water dominant kerogens, implying that the different nitrogen-fixation pathway between the shallow- and deep-water ecosystems. Such difference is most likely related to extremely high productivity of cyanobacteria in the shallow part.

All of data suggest that ecosystem at ca.1.9 Ga was more-strongly concealed with (1) local tectonics (thus, rifting environments), (2) atmospheric chemistry (relatively high CO₂), (3) temporal supply of elements (supply of iron and phosphate) and (4) redox conditions of oceans.

Re-Os isotopes and platinum-group elements in a peridotite-pyroxenite hybrid mantle

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Melting of a peridotite-pyroxenite hybrid source has been proposed to explain varied petrological and geochemical characteristics of mantle-derived magmas. Re-Os isotope systematics in OIB provide strong evidence for the presence of recycled components in their sources. However, Os isotope variations in OIB (¹⁸⁷Os/¹⁸⁸Os < 0.16) are restricted relative to the predicted compositions for recycled crust (¹⁸⁷Os/¹⁸⁸Os ~9 for 1 Ga basalt). It is unclear whether this observation reflects lesser contributions from recycled components as a result of effective reaction with ambient peridotite shortly before eruption, or if it is due to modification of Re-Os budgets in recycled crust during subduction and mantle convection [1]. We present Re-Os isotope systematics and platinum-group element (PGE) abundances for a xenolith suite of 8 garnet clinopyroxenites and 7 garnet orthopyroxenites from Malaita, Solomon Islands. Geological, petrochemical, and thermobarometric evidence indicate that they represent a series of melting residues of a hybrid source located within the oceanic asthenosphere [2]. Neoproterozoic formation of the protolith has been suggested on the basis of Sr-Nd-Hf-Pb isotopes of garnet clinopyroxenites [3]. Thus, the primary aim is to test whether recycled pyroxenites are capable of preserving large Os isotope anomalies in the convective mantle. In addition, we address the origin of clino- and orthopyroxenites using PGE characteristics.

The two lithologies display contrasting ¹⁸⁷Os/¹⁸⁸Os ratios and PGE patterns. Clinopyroxenites possess highly radiogenic ¹⁸⁷Os/¹⁸⁸Os ratios ranging from 0.17 to 5, and are characterized by basalt-like, positively sloped PGE patterns. In contrast, most orthopyroxenites have unradiogenic ¹⁸⁷Os/¹⁸⁸Os ratios extending as low as 0.12, and tend to show peridotite-like, unfractionated PGE patterns. This suggests that these two contrasting lithologies largely retain the memory of their respective sources because of the relative immunity of PGE signatures to post-crystallization disturbance such as dehydration in the subducting slab, diffusion in the convective mantle, and even melt-mediated hybridization in upwelling mantle.

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First-principles exploration of crystal structures of pure iron and iron-silicon alloy at Earth's inner core pressures

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Recent experimental and theoretical studies have revealed that many simple elements have complex crystal structures with low symmetry at high pressures [1]. One of the examples is calcium, which is the alkali earth metal bordering the 3d-transition metal on the periodic table. It was found that the electrons of 4s-character decrease with pressure, while those of 3d- increase. Then calcium behaves like the 3d-transition metal under high pressure. In the condition, calcium takes very complex crystal structures. It has a face-centered cubic (fcc) structure (Ca-I) at ambient condition and transforms to a body-centered cubic (bcc) structure (Ca-II) at 20 GPa, then to a simple cubic structure (Ca-III) at 32 GPa. By further compression, Ca-IV (113-137 GPa) and Ca-V (137 GPa) emerge [2], each of which has a complex crystal structure. Both Ca-IV and Ca-V have a coordination number of 7. The structure of Ca-IV is a four-fold helical structure and that of Ca-V a zigzag structure [3,4]. These facts suggest a possibility that iron, which is a 3d-transition metal and a primary constituent of the Earth's inner core, would also have the complex crystal structures in high pressure conditions.

In this study, we investigate the validity of this hypothesis by applying the complex crystal structures of calcium to iron and examining the relative energy differences among the candidate structures. In addition to the calculations of pure iron, we also investigate the effect of silicon incorporation on the appearance of complex crystal structures in highly compressed iron.

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Metals in oxidized and metasomatized peridotite xenoliths derived from the mantle wedge

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Relatively high oxidation state has been well known as one of the main character of mantle-wedge peridotites [1, 2], and interpreted as a result of the supply of slab derived materials (fluids and melts) [2]. Residual mantle peridotite xenoliths from Avacha volcano, on the volcanic front of southern Kamchatka arc, are characterized by SiO₂-addition through the reaction with slab derived fluids and melts. Most of the Avacha peridotites show highly oxidized conditions ($\Delta\text{FMQ} = -0.2$ to $+2.0$). But we found several native metals and alloys, i.e. native Ni, native Fe, Fe silicide (Fe-Si-Ti alloy) and possible native Ti, as inclusions in such oxidized and metasomatized peridotite xenoliths (samples #159, #166 and #679). In addition, #159 also contains several grains of FeAs₂ (löllingite) [3] and a large amount of sulfides [4] as inclusions, and sulfides are not altered to any secondary minerals [4]. Three grains of Fe-Si-Ti alloys are found in #159 and #166, and the grain in #166 show an inhomogeneous element distribution as a kind of sector zoning although other grains in #159 are homogeneous in chemistry. The two Fe-Si-Ti alloys in #159 show Fe₅₄Si₄₀Ti₆ and Fe₃₀Si₇₀ in chemistry, and the former is almost the same as the most Fe-rich part of the grain in #166.

The metals and alloys form inclusion trails with other minute inclusions (probably fluid(s)) in relatively coarse mantle minerals. The Fe-rich silicide in sample #159 forms an inclusion trail with pyroxenes in olivine. This possibly indicates the transportation of Si and Ti by an extremely reduced fluid or melt (but not sulfide melt) within relatively oxidized mantle wedge. Our finding implies the possibility of solubility of Ti to aqueous fluid although not indicated theoretically or experimentally.

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Spatial and temporal variability of magmatism at the northern end of the Mariana Trough - Interactions between arc magmatism and nascent rifting

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The southern end of the Izu-Bonin arc and northernmost part of Mariana arc are characterized by highly alkaline shoshonitic lavas, referred to as the alkalic volcano province (AVP) (e.g., Bloomer et al., 1989; Sun and Stern, 2001; Ishizuka et al., 2007). These compositions are unusual for intra-oceanic arcs. Back-arc and intra-arc rifting forming Mariana Trough is propagating northward through this area, while back-arc spreading and creation of oceanic crust has not begun. This area coincides closely with the location of shear wave speed anomalies in the mantle wedge (Isse *et al.* 2009).

Dredge sampling along the northern tip of Mariana Trough (West Mariana Ridge: WMR) recovered exclusively medium K to shoshonitic basalts. These basalts have significantly higher alkali contents than Mariana Trough basalts, and show clear arc-like signatures. High-precision Pb isotopic analyses reveal that the monogenetic volcanoes form a single trend on Pb-Pb isotopic plots between 2 components, one with lower ²⁰⁶Pb/²⁰⁴Pb and high $\Delta 7/4$, and another with high ²⁰⁶Pb/²⁰⁴Pb as well as low $\Delta 7/4$ and $8/4$ (HIMU-like). These components could correspond respectively to subducted pelagic sediment and subducted HIMU seamounts.

Age of shoshonitic lavas systematically becomes younger toward north. The age of c. 6Ma was obtained at 21.5°N, c. 3 Ma at 23-23.5°N, and zero-age shoshonites occur on Ioto Island at 24.4°N. This implies that shoshonitic magmatism represents the leading edge of rifting and is propagating northward with time. Older (12-10 Ma) rear arc volcanoes west of the WMR are not shoshonitic, but still have higher ²⁰⁶Pb/²⁰⁴Pb compared to the rear arc volcanoes to the north, implying that high ²⁰⁶Pb/²⁰⁴Pb (HIMU-like) subducting component existed prior to onset of alkaline magmatism.

We will test whether alkaline magmatism in this area is caused purely by mantle process associated with rifting or induced by variation of subducting material.

Variations in the redox state of As and Fe measured by X-ray absorption spectroscopy in aquifers of Bangladesh and their effect on As adsorption

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Groundwater contamination by naturally occurring arsenic (As) is a very serious problem. In Bangladesh, household well waters contaminated by As generally show a large variation of As concentration even throughout a small village. This variation creates a difficulty in the design of mitigation strategies. We hypothesized that the concentration of As in each well is controlled by an adsorption-desorption equilibrium between sediment and groundwater. To verify the hypothesis, two factors are focused upon in this study: (i) speciation of As and Fe in the solid phase, and (ii) the adsorption properties of As(III) and As(V) to sediment. Sediment core samples were collected from an As-contaminated aquifer at Sonargaon, central eastern Bangladesh. The oxidation states of As and Fe in the sediments as determined by X-ray absorption near the edge structure (XANES) showed a distinct redox boundary below 5 m from the ground surface, whereas the peak of dissolved As is observed below 15 m. The apparent distribution coefficient ($K_d = C_{\text{solid}}/C_{\text{solution}}$) of As(V) is always larger than that of As(III) at all the depths. A simulated concentrations of As in the groundwater obtained by multiplying the amount of P-extracted As and K_d^{-1} with considering the oxidation state of As is consistent with depth profile of As in groundwater. This suggests that the concentration of dissolved As is strongly controlled by an adsorption-desorption equilibrium between sediment and groundwater. Variation in K_d is basically controlled by oxidation state of As and the concentration of Fe oxyhydroxides. The discrepancy between the depth of the redox boundary and the peak of dissolved As is attributed to the difference in abundance of P-extracted As rather than to a variation of K_d . The adsorption equilibrium model proposed in this study can be applied to the quantitative evaluation of the great variation in aqueous As concentration in groundwater from Holocene aquifers.

Earth system model study of potential response of marine OC aerosols to ocean ecosystem changes

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Model approach

It has been proposed that the marine biogeochemical sulfur cycle could stabilize the Earth's climate against perturbations by exerting a negative feedback on climate [1]. Recent findings of significant amounts of organic matter in the sub-micrometer aerosols have suggested that the insoluble organic aerosols are the dominant source for the marine aerosols during periods of increased biological activity in the ocean [2]. This work investigates the effects of ocean ecosystem changes on the marine organic carbon (OC) fluxes by using an integrated Earth System Model. We perform four different scenarios (Sc1–4) to investigate the effects of ocean ecosystem changes on the marine OC flux (Table 1).

Scenario	Chlorophyll Data	Condition of Chlorophyll
Sc1 ^a	Model	Preindustrial time
Sc2 ^b	Satellite	Present (2003–2007)
Sc3 ^c	Model	No effect on OC
Sc4 ^d	Model	Future (2080–2100)

^aControl run with marine OC emissions.

^bSensitivity run with marine OC emissions constrained by the satellite observations of chlorophylls.

^cSensitivity run without marine OC emissions.

^dSensitivity run with marine OC emissions due to triple CO₂ concentrations.

Table 1: Summary of different simulations performed.

Discussion of results

Our modeled estimate of global marine primary OC emission is comparable with that constrained by the satellite observations of chlorophylls. Our estimates of enhancements in the modeled OC concentrations due to the marine sources are consistent with previous measurements of water-insoluble organic carbon in summer over the open ocean. We find the significant increase in the averaged surface OC concentration in September over the Arctic ocean (70–90°N), which is largely driven by the disappearances of sea-ice cover due to triple CO₂ concentrations. Our results imply that future OC increases over Arctic Ocean may affect the climate feedback.

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Accumulation of iodine on Andosol

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Iodine is an essential element for human and plays an important role in thyroid gland function. Long lived radiiodine, ¹²⁹I (half-life:1.6x10⁷y), is released from nuclear facilities and atmospheric nuclear weapons test. This nuclide is expected to accumulate in soil and behave together with stable iodine (¹²⁷I). Therefore, it is important to study the levels and behavior of both stable and ¹²⁹I in the soil environment. In this study we have analyzed concentration of iodine in soil samples by ICP-MS and ¹²⁹I by AMS. We also carried out sorption experiments to understand the accumulation mechanisms.

Analytical results for different soils collected in Japan showed that iodine levels were in the range about 1–50ppm (dry basis). Markedly high iodine concentrations of about 20–50ppm were found in Andosol, volcanic ash soil with high organic contents. Since the parent materials (e.g. basalt and andesite) contain low iodine (about 0.05ppm), this element would be accumulated in Andosol more than several hundred times. Vertical distribution of ¹²⁹I showed that this nuclide was highly accumulated in surface soil (6x10⁻⁴Bq/kg) compared to that in the lower layers. This suggests that anthropogenic ¹²⁹I is strongly associated with soil constituents.

Results for the sorption experiments (batch experiments) showed that the sorption percentage for I⁻ differ significantly between the upper and lower layers. The values of I⁻ for fresh soils were 96% for upper layer and 17% for lower one. In case of IO₃⁻, the sorption percentages for both upper and lower layers were high (about 94%). These results indicate that the sorption is highly dependent on the chemical forms of iodine.

To examine the effects of microorganisms on the sorption, soil samples were treated by autoclaving and heating at different temperatures prior to the experiments. Adsorption of I⁻ was substantially reduced by autoclaving and heating treatments, while the IO₃⁻ sorption was not so much influenced by such treatments. This suggests that microorganisms seem to be important in the sorption of I⁻.

We also studied desorption of iodine from soil under flooded conditions. Iodine was desorbed from soil into soil solution under reducing conditions (low Eh) created by the activities microorganisms.

Multielement profiling analyses of seawater in coral reef area and the biogeochemical processes of trace metals in bivalve with symbiotic zooxanthellae

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In coral reef area, a characteristic ecosystem is formed by many kinds of marine animals and plants in spite of uneutrophic conditions. This may be attributed to the fact that various chemical species are effectively taken and available by lower animals and plants. A symbiotic relationship often found among different animals and plants is considered to be working as one of such processes. In a present study, firstly, multielement determination of major-to-ultratrace elements in seawater and each organ of bivalve with symbiotic zooxanthellae (*Tridacna crocea*) were carried out by ICP-AES, ICP-MS and CHN coder. Secondly, the biogeochemical processes of trace metals in *Tridacna crocea* were investigated by the laboratory experiments using stable enriched isotopes of ^{111}Cd and ^{68}Zn .

The analytical results for seawater showed that the concentrations of the bioactive elements such as Co, Ni, Cu, Zn, Cd, and Pb were in the range from 0.5-5 fold, compared to the literature values [1, 2] for open surface seawater. From the multielement profiles for nutrient type elements, it was suggested that the concentrations of Zn and Cd in seawater normalized to open surface seawater were higher than those of Ni and Cu. In the laboratory experiment about *Tridacna crocea*, the ratios of ^{68}Zn to other Zn isotopes increased with time for the mantle, in which symbiotic zooxanthellae exist, but they showed almost same with natural abundances for the kidney, while the ratios of ^{111}Cd to other isotopes showed the highest for the kidney among all organs. These results suggested there are the difference of bioavailability between Cd and Zn.

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Zygote isotopy and the epigenetic code

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Self-sufficiency and self isolation of the zygote cleavage process is a unique peculiarity specific for a whole diversity of multicellular life forms. That means, the complete circle of primary embryogenesis stage does not require a special biological environment. An appropriate physic-chemical conditions are the only requirements need to promote this process. Once these conditions maintained, a normal embryogenesis is to processed. This makes possible to study this process in vitro which itself is a unique possibility for further epigenesis research since this particular embryogenesis step leads to the beginning of the genetically unified embryonic cell differential determination. Epigenetic directions for selective reading of DNA information in differently specializing cells derives from their individual development programs which fits perfectly their functional patterns. There are up to some hundred programs of that sort in one single organism. Thus, a zygote possesses a high potential of directing programs that caused by the top-regularity mechanism for its reproduction throughout a long chain of generations of the wide majority of organisms. It is known that the selective methylation of several DNA loci regulates genome expression, i.e. performs the gene expression epigenetic control. However, an exact mechanism of this regular methylation selectivity still remains obscure.

The biological isotope fractionation research revealed a non-random character of both intermolecular and intramolecular isotopes distribution in biological processes [1]. This was taken as a basis for study on distribution of ectopically different nucleotide forms in blastomer DNA during the zygote cleavage [2,3]. The data obtained reveals a non-random and a high-order character of distribution of isotopically different nucleotide forms between complementary chains in DNA double helices. Noteworthy, the high order comes due to the zygote cleavage circle self-isolation and therefore such an algorithm would be relevant for all multi-cell life forms as well. Owing to the work of different kind of effects, a differential distribution of isotopically different nucleotide forms in blastomer DNA should lead to a selective DNA methylation. The latter could be a background of the very nature of epigenetic code.

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Surface exposure dating of large landslides in the European Alps: Wildalpen (Styria, Austria)

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We are surface exposure dating boulder and bedrock surfaces from large prehistoric landslides in the Alps. In addition to determining the ages for landslides whose ages are unknown, we are examining cosmogenic nuclide production rates based on results from landslides with independent age constraints. We focus on ¹⁰Be, ²⁶Al in crystalline regions with abundant quartz, while ³⁶Cl is used in areas underlain by calcareous rocks. Potential complications include pre-exposure, post-slide rock fall, and shielding by soil or snow, as well as weathering of boulder surfaces. Here we focus on the Wildalpen landslide in the Hochschwab region of Styria (Austria). The Wildalpen landslide involved the movement of about one cubic kilometer of Wettersteinkalk, with a run-out of 12 km. Radiocarbon dating of trees entrained in the slide point to an age of about 6 ka cal BP [1]. We sampled and analyzed ³⁶Cl in ten boulders from three different parts of the slide mass. ³⁶Cl exposure ages and production rates calculated based on the formalism presented by Alfimov and Ivy-Ochs [2] will be discussed.

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$\delta^{53}\text{Cr}$ mixing, fractionation and exchange in contaminant plumes

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Cr (VI) concentrations in contaminant plumes in alkaline, oxic aquifers in the Mojave Desert near Topoc, Hinkley, and El Mirage, Calif., were as high as 6,600, 2,600 and 330 $\mu\text{g/L}$, respectively. $\delta^{53}\text{Cr}$ compositions from more than 50 samples collected within these plumes ranged from near 0 per mil to almost 4 per mil near the plume margins. Assuming only reductive fractionation of Cr (VI) to Cr (III), apparent fractionation factors (α) for Cr-52 and Cr-53 isotopes were 0.993 within the Topoc and Hinkley plumes, and only the El Mirage plume had an α value similar to the laboratory derived value of 0.9965. One possible explanation for the difference in fractionation factors is advective mixing near the plume margin prior to reductive fractionation. All three plumes show evidence of mixing of native and contaminated ground water near the plume margin and subsequent reductive fractionation. Only the El Mirage plume had significant Cr (III) concentrations, comprising as much as 20 percent of the total dissolved chromium, within the core of the plume that were indicative of chromium reduction prior to mixing with native ground water. In addition to advective mixing of native and contaminated water, $\delta^{53}\text{Cr}$ data suggest that exchange of dissolved Cr (VI) with Cr (VI) sorbed to the surfaces of the mineral grains altered the $\delta^{53}\text{Cr}$ composition of the sorbed chromium. As a consequence of exchange reactions, $\delta^{53}\text{Cr}$ compositions near 0 per mil were present in areas having low (background) Cr (VI) concentrations that had been previously exposed to contaminated water.