

Modeling Fe-Ni metal and silicate melt compositions produced by thermal reduction of nebular condensates above the liquidus

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The revised version of the METEOMOD model [1, 2] allows simulations of the compositional evolution of the Fe-Ni metal exsolved from protochondritic liquids during equilibrium heating above the silicate liquidus. Results of preliminary calculations have demonstrated a similarity between the calculated proportions and compositions, and those observed in LL to H chondrites [3]. This led us to a fundamental conclusion that differences in the nebular redox conditions may play a subordinate role in the formation of the main components of ordinary chondrites. Due to the highly endothermic nature of the $\text{FeO}_{\text{melt}} \rightarrow \text{Fe}^0 + 0.5\text{O}_2$ reaction, the presence of a reducing agent (carbon, hydrogen gas) is not required to reduce large amounts of metal from silicate melts during a flush heating event over 1600-1800°C. To constraint the hypothesis numerically, we performed low-pressure calculations simulating thermal reduction of primordial dust-enriched solar nebular condensates [4] which composition was derived from the CWPI program [5]. The simulation has been carried out on mineral assemblages condensed at 1000-1200°C and then completely melted above the olivine liquidus in the range of ~1550-2100°C at a constant oxygen fugacity ($\log f_{\text{O}_2} = -6.5$). As a result, a sequence of expected equilibrium low FeO to almost iron-free melt compositions were generated displaying a complimentary increase in SiO_2 and mg#. A non-trivial result of this modelling includes relations between the calculated amount of metal and its Ni/(Ni+Fe) ratios that were found to be similar to the average characteristics of the metal phase observed in the ordinary LL, L, and H chondrites [6]. This argues that a flush increase of temperature may be the main factor differentiating the nebular source into a primary metallic phase and molten silicate (chondrules?) residues that have been evolving to more reduced and magnesian compositions.

[1] Ariskin *et al.* (1997) *Met. Planet. Sci.* **32**, 123-133.
[2] Bychkov *et al.* (2006) *Abs. 69th Met. meeting.* [3] Ariskin *et al.* (2006) *Ibid.* [4] Anders & Grevesse (1989) *GCA* **53**, 197-214. [5] Petaev & Wood (2005) In: *ASP Conf. Ser.* **341**, 373-406. [6] Schaefer & Fegley (2007) *Icarus* **186**, 462-483.

Structure of MgSiO_3 glass at high pressure and temperature

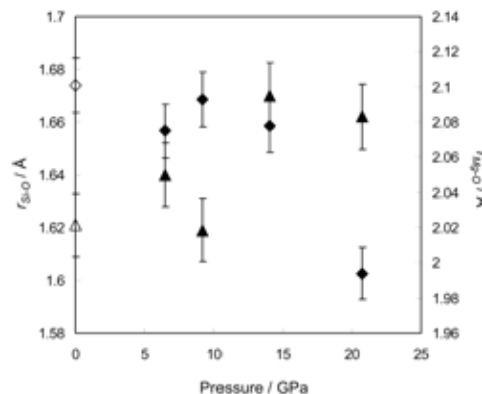
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X-ray diffraction studies of vitreous MgSiO_3 (*v-En*) were performed at BL04B1 at SPring-8 and ARNE5C at KEK using 6/8 and cubic-type multianvil devices up to 21 GPa and 863K. Energy dispersive patterns were obtained with a polychromatic X-ray beam (30-180 keV) at diffraction angles (2θ) between 3° and 25°. Samples were compressed cold and diffraction data collected prior to heating and at successively higher temperatures until crystallization was encountered. The figure below presents the interatomic distances for Si-O (triangles) and Mg-O (diamonds) for *v-En* just below the crystallization temperature at 6.5, 9.2, 14 and 21 GPa. Open symbols represent interatomic distances for 1 atm. Si-O and Mg-O bond lengths show broadly antithetic variations with pressure. The average Si-O increases and Mg-O decreases from 0 to ~7 GPa, followed by a reversal up to ~11 GPa. At higher pressures the Mg-O bond shortens and Si-O bond initially lengthens and then may decrease. Raman spectroscopy shows permanent changes in structure for glasses recovered from above 6.5 GPa, consistent with the development of a more depolymerized silicate network.



We interpret these variations as reflecting changes in topology related to compression of the Si and Mg polyhedra and coordination changes. The increase and decrease in Si-O and Mg-O bond lengths, respectively, above ~10 GPa are consistent with an increase in Si coordination and accompanying collapse of Mg polyhedra. The production of high coordinated Si is supported by the recent NMR study of Gaudio *et al.* [*GCA*, 2008, 72] reporting ²⁹Si and ²⁹Si in *v-En* after heating at 10 GPa and rapid decompression. NMR studies underway on annealed glasses decompressed from >10 GPa will further aid in the interpretation of our diffraction data.

New (U-Th)/He dating systems and ages in Japan Atomic Energy Agency

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Japan Atomic Energy Agency has jointly set up the system of the (U-Th)/He dating in cooperation with Kyoto University and National Institute for Earth Sciences and Disaster Prevention. Through these two years, helium extraction machine using an electronically-cooled diode laser, micro crucible system using XRF bead sampler and uranium and thorium quantification procedure without artificial spikes are developed. Now we produce new ages of some age known samples. At the present stage, the accuracy and precision are roughly 20 and 10%, respectively, using the age standard zircon from the Fish Canyon Tuff (FC3). In the presentation, we will introduce our systems and the ages in detail.

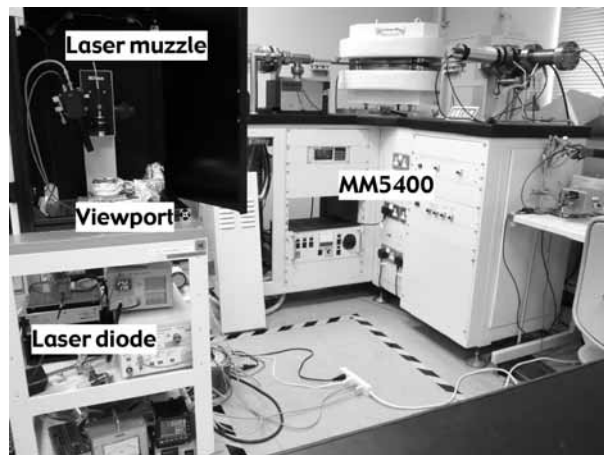


Figure 1: Helium extraction machine and MM5400 mass spectrometer.

Late Cenozoic magmatic evolution in the NE Honshu arc

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The NE Honshu magmatic arc was formed through back-arc spreading (21-19Ma), subsequent multiple rifting (18-13.5 Ma), and island-arc uplifting (13.5 Ma to the present) stages after continental margin volcanic period. The volcanic activities have evolved from andesites in terrestrial condition, submarine basalt flows and bi-modal volcanic activity in rift zones, caldera-forming silicic eruption in a shallow water to terrestrial environment, and lastly subaerial andesitic volcanism. Back-arc spreading and subsequent rifting created eight petro-tectonic associations; the Yamato Basin, three sets of Horst-Graben zones and the fore-arc range. The volcanism in the back-arc period gradually changed its composition from west to east with time. MORB-like basalts were dominant in the west, through back-arc basin basalts were dominant in the midway, and bi-modal volcanism with abundant silicic volcanics became dominant with subordinate island-arc type basalt in the east. The strongly depleted magma source intruded into the back-arc side at about 20 Ma and the interaction with more fertile source has been continued to 16 Ma in the Aosawa rift area, then weakly depleted source originated primary basalts in the Babame and Kuroko Rifts during 16-13.5 Ma.

Large volume of silicic volcanism occurred at the final stage of the back-arc rifting. The rhyolites related with rift formation are characterized by aphyric feature with higher HFS elements than the later quartz-phyric silicic magmas from the island-arc stage. The rifting-stage high temperature rhyolites must be derived from relatively deep seated magma chambers than the island-arc stage rhyolites with hydrous phenocrysts. During the later island-arc stage, the magmatic temperature at volcanic front was falling down with time, and lastly hornblende-phyric low-K andesites erupted.

Systematics on the stability constants of REE-humic complexes at various metal loading levels

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The stability constants of rare earth elements (REE) with humic substances (HS) have been widely studied to predict the behavior of REE in natural waters. It is well known that the apparent stability constant (β_{M-HS}) of metal cation with HS depends on various parameters such as pH. There are differences in not only the absolute value but also relative shape of REE pattern of the β_{M-HS} among previous studies [1-5]. This difference in the relative shape could be explained by change of the main binding site of REE in HS due to the variation of REE loading in HS. However, it has not been confirmed yet in a series of experiments where relative shape of REE pattern of the β_{M-HS} can change with the variation of REE loading in HS. In order to understand the systematics on the β_{M-HS} of REE-HS complexes with the variation of REE loading, we determined the β_{M-HS} of all REE (except for Pm) at various REE loading levels using solvent extraction, equilibrium dialysis, and ultrafiltration methods.

The β_{M-HS} using solvent extraction has a peak around middle REE part at higher REE loading, while the REE pattern shows a monotonous increase from La to Lu at lower REE loading. On the other hand, the variation of relative shape of the REE pattern is not found in the β_{M-HS} using equilibrium dialysis. By comparison with previous studies, it is suggested that abundance of major multivalent cations originally included in HS such as Fe^{3+} can control the variation of relative shape of REE pattern of the β_{M-HS} .

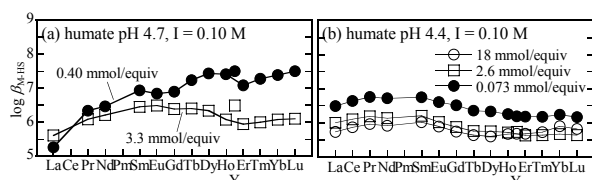


Figure 1: Log β_{M-HS} of humate using (a) solvent extraction and (b) equilibrium dialysis.

- [1] Tang & Johannesson (2003) *GCA* **67**, 2321-2339.
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Estimation of recharge water flux into confined aquifer system in northeastern Osaka Basin, Japan

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The objective of this study is to estimate recharge water flux into confined aquifer system in Northeastern Osaka Basin (NEOB), where the system is well developed, by using mass balance method based on cation exchange reaction.

Shallow confined groundwater (above depths of 100m) in the NEOB modified its chemistry from Ca-HCO₃ type through Mg-HCO₃ type to Na-HCO₃ type along the flowpaths. Areas with the water types are expressed as zones A, B, and C, in that order. In addition, exchangeable cation (EXC) in clay layers distributes in concordant with the cation of the groundwater and the NEOB had suffered transgression in the past. These facts indicate that distributional patterns of both cation compositions reflect adsorption affinities of the cations onto clay. Namely, the EXC of clay layers had been fairly enriched in Na and Mg with marine origin right after the regression, and then, had released Na and Mg in turns by cation exchange reaction with Ca-HCO₃ type recharge water. As the consequent of such a displacement chromatography for a long-term period, it is considered that cations of both groundwater and EXC have been spatially distributed in turns of Ca type, Mg type and Na type from the recharge area to down-flow area.

We tried to estimate a necessary amount of natural recharge to differentiate the EXC after the latest regression. It is assumed that Na-X and Mg-X₂ of EXC (X: exchange substrate) have been exchanged by Ca originated from recharge water since the regression. By using the distributional pattern of EXC, the period of the recharge, Ca contents of recharge water and parameters of clay layers such as thickness, bulk density and cation exchange capacity, the flux of recharge water into the confined aquifer system according to this chromatographic model is estimated to be 0.99 mm/day, which is compatible with the average recharge flux to unconfined groundwater in Japan (1 mm/day).

Unique shallow-water hydrothermal system associated with submarine volcanism in the Aira caldera, South Kyushu, Japan

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Shallow submarine hydrothermal activities were confirmed in the seafloor at 200 m water depth within the Wakamiko crater (31°40'N, 130°46'E) in Kagoshima Bay, south Kyushu Japan. This crater is considered a main crater of the Aira caldera, which is formed as a result of last huge eruption about 2.5ka. This area is also known active fumarolic gas discharge, suggesting the Aira caldera is still an active volcano. Fluid and sediment samples have been extensively collected during dive programs using ROV/HyperDolphin and surface ship surveys using Tansai-Maru of JAMSTEC, and studied to reveal geochemical signature of the hydrothermal and fumarolic activities.

In the northwest area of the crater, high temperature active fluid venting (Tmax = 200°C) was discovered in June, 2007 [1]. White patch area nearby the vent field was observed, where the pore fluid chemistry shows mixing between the ascending hydrothermal fluid and seawater [3]. On the other hand, weak fluid emanation from a hydrothermal mound was observed in the east area [2]. Occurrence of montmorillonite in the mound sediment is considered as not stable for the present pore fluid chemical composition, which may be a result of fluctuation of fumarolic gas flux through the surface sediment [3].

In addition, fumaroles are extended out of the crater, the atop of knoll adjacent to the crater is one of the active areas. *Vestimentiferan* tube-worms inhabit near the fumaroles at 100 m water depth. It is inferred that they depend on the gas flux instead of the hydrothermal fluids.

[1] Yamanaka *et al.* (2007) *EOS Trans. AGU*, **88(52)** Fall Meet. Suppl., Abstract V21D-0756. [2] Ishibashi *et al.* (2008, in press) *J. Volcanol. Geotherml. Res.* [3] Nakaseama *et al.* (2008, in press) *Resource Geology*.

Collapse of the Songpan-Ganze Orogenic belt and Mesozoic mid-crustal ductile channel flow: Evidence from the Longmenshan foreland thrust belt

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The early Mesozoic orogeny in the Songpan-Ganze region, SW China produced crustal thickening (~50–60 km), followed by regional extension and crustal thinning. The regional extension involved ductile deformation and metamorphism of the Sinian-Paleozoic strata around extensional domes within the Longmenshan area. This extensional deformation removed or selectively thinned the strata. The deformed rocks are marked by ductile shear zones, bedding penetrative foliation and mineral lineation. The kinematic markers indicate SSE- or south-ward motion in the northern part of Longmenshan and SE-ward motion in the middle and southern sections. The mylonitic rocks have greenschist to low amphibolite facies mineral assemblages and P-T conditions in the Silurian Maoxian group are estimated to have been 265–405°C and 0.31–0.48 GPa, consistent with a mid-crustal ductile channel flow. Previous studies placed the age of metamorphism at 190–150 Ma using ³⁹Ar/⁴⁰Ar and SHRIMP U-Pb methods. We conclude that the thickened crust was thinned by mid-crustal ductile channel flow, which then led to collapse of the Mesozoic Songpan-Ganze orogenic belt.

Geochronology and geological implications of the Mengku plagiogranite pluton in Altay, Xinjiang

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The Altai Mountains are a key area for understanding the development of the Altai Tectonic Collage and accretionary orogen. In this work, we undertake zircon U-Pb dating of two Paleozoic synorogenic plutons in order to better define the early magmatic and tectonic evolution of the Chinese Altai Mountains. SHRIMP U-Pb zircon dating on the Mengku plagiogranite pluton in the Mengku iron deposit district in Xinjiang shows that it was formed at 400 ± 6 Ma (MSWD=1.3). This age is similar to biotite granite at the north part of the No. 1 orebody (SHRIMP U-Pb dating is 404 ± 8 Ma), indicating that they were formed at the beginning of the Early Devonian.

The Altay area is an important metallogenic province characterized by Early Devonian Kangbutiebao Formation marine volcanic rocks hosting Cu, Pb, Zn and Fe deposits. However, the absolute timing of Kangbutiebao Formation cannot be well constrained by the isotopic dates. These plutons intrude Kangbutiebao Formation, showing that Kangbutiebao Formation could have been much earlier than 404 Ma. We think that the Kangbutiebao Formation formed in the Late Silurian. The Mengku large scale iron deposit is related to magmatic hydrothermal activity, and the ages of the plutons shows that iron mineralization formed in slightly later than 404-400 Ma.

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From back-arc basin to back-arc foreland basin: Evidences from trace and Rare Earth Elements of the Early Ordovician and Early Silurian sandstones of Jingtai, Eastern North Qilian, China

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The Early Ordovician and Early Silurian are the key periods for the evolution of tectonics in North Qilian Caledonian orogenic belts. The trace and rare earth elements of sandstones from Lower Ordovician Yingou Formation and Lower Silurian Angzanggou Formation in Jingtai area were presented. The samples from lower part of Yingou Formation are characteristic of minimal Eu/Eu* (0.54) and maximal Th/Sc (2.05), Σ REE (204.38), and contrast with the middle-upper part of Yingou Formation possessing maximal Eu/Eu* (0.91) and minimal Th/Sc (0.07), Σ REE (41.63), and intermediate Eu/Eu* (0.62), Th/Sc (1.21), Σ REE (164.43) for those of Angzanggou Formation. Diverse plots of provenance and tectonic setting discrimination and multi-element diagrams show that (1) the lower part of Yingou Formation is mainly derived from recycled sedimentary and felsic sources positioned in continental margin and other recycled terrigenous sediments with a comparable property to the former; the middle-upper part indicates a dominate derivation from mafic-andesitic sources in a island arc environment, and is corresponding to the early stage of Shihuigou Arc; (2) the tectonic setting of Anagzanggou Formation is delusive caused by the coexistence of continental island arc, active continental margin and passive continental margin due to the mixing of the detritus from these provenances, and may source from the metasedimentary rocks locating in the south margin of Alashan Block, the island arc volcanic rocks with middle-high maturity in Shihuigou area and the ancient metavolcanic rocks. The results suggest an evolution from back-arc basin of the Early Ordovician to back-arc foreland basin in the Early Silurian.

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Age and growth of the Archean Kongling terrain, South China, with emphasis on 3.3 Ga granitoid gneisses

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Zircon U-Pb ages and Hf isotopic compositions of granodioritic-trondhjemitic gneisses and metasedimentary rocks from the Kongling terrain were analyzed by LA-ICP-MS and LA-MC-ICP-MS. Magmatic zircons from two granodioritic and trondhjemitic gneisses from the northern Kongling terrain yield a major age group in the range of 3.1-3.3Ga. Five oldest igneous zircons from this group give a weighted average ²⁰⁶Pb/²⁰⁷Pb age of 3300.8±8.4 (2σ, MSWD=0.15), which is interpreted to represent the age of magmatism. Thus, they represent the oldest known rocks in South China. Igneous zircons in one trondhjemitic gneiss from the southern Kongling terrain yield a weighted average ²⁰⁶Pb/²⁰⁷Pb age of 2981±13Ma (2σ, MSWD=9.7, n=21). The results reinforce that magmatism of the whole Kongling terrain mainly occurred at 2.9Ga. Two quartzites and one metapelite from the southern Kongling terrain give concordant major age groups of 2670±4 Ma, 2684±26Ma and 2911±19Ma.

Two-stage Hf model ages suggest that the majority of the Kongling crust formed between 3.2 and 3.8Ga. Significant magmatism at 3.3 and 2.9Ga may represent mantle additions into the pre-existing older crust.

The metasedimentary rocks show coupled negative Eu and Sr anomalies. The negative Eu anomalies (Eu/Eu*=0.53-0.75) are similar to post-Archean shales. We suggest that in addition to the K-rich granitic and rhyolitic materials, preferential decomposition of plagioclase can also lead to negative Eu anomalies in Archean sedimentary rocks. Therefore, Eu anomaly as indicator of crustal evolution should be used with caution.

Palaeoclimate variation during Pleistocene and Holocene in the Northern Jiangsu Plain, East China: Geochemical and isotopic proxies from the Baoying borehole

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The Baoying borehole was drilled in the Wangzhigang Town of Baoying County (33°14'21"N, 119°22'41"E) in the Northern Jiangsu Basin with recovery of 96.81m of clay and silty sediment samples. Sedimentary facies of the core show a series of environmental changes from coastal bay of a shallow sea upward to a wide alluvial plain during Pleistocene and Holocene time. A comprehensive study of the geomorphology, structure, sedimentary facies, minerals, chemical and isotopic analyses, paleomagnetic and paleo-microfossil analyses have indicated a fluvial-marine interaction during the evolution of the plain since 2.58 Ma.

In this study, a number of geochemical proxies have been developed in an effort to extract climatically sensitive data from the sediments in the land-sea interaction zone. The depth profiles of CIA (chemical index of alteration), Fe/Mn, Rb/Sr, TOC/TN, δ¹³C_{TOC} and δ¹⁵N in the sediments exhibit climate-controlling patterns which correspond significantly with proxy-climate records of ODP1143 δ¹⁸O curves and Luochuan loess magnetic susceptibility (MS) curves. This is indicative that the sediments of the Baoying borehole have preserved basically the palaeoclimatic records through elemental and isotopic parameters with the same MIS recorded in the benthonic δ¹⁸O records. The combination of above geochemical and isotopic proxies for the Baoying sediments can be used as proxy-climate references for variations in the coastal area. In conclusion, it is clear from multiple lines of evidence that the evolutionary history of the inner part of the Northern Jiangsu Plain is characterized by fluvial-marine interactive events during Pleistocene and Holocene.

Kinetics of Fe(II)-catalyzed transformation of ferrihydrite under anaerobic dynamic flow conditions

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The reduction of iron oxides, both biotically and abiotically, is one of the most important chemical processes for cycling of iron in the environment and has a profound influence on the mobility of soil and groundwater contaminants. The ferrous ions produced during this process will be absorbed onto the surfaces of remaining Fe-hydroxides, which play an important role in controlling the subsequent transformations of host Fe-hydroxide minerals. However, the detailed mechanisms, pathways and kinetics of such Fe(II)-catalyzed transformation of Fe-hydroxides is still unclear, especially under dynamic flow micro-porous subsurface environment.

To better understand this process, an inorganic ferrous ion solution was directly injected into 100 μm I.D. capillary tubes packed with ferrihydrite coated glass spheres under anaerobic circumneutral pH conditions to study the kinetics of secondary mineral transformations from ferrihydrite in flow through micro-porous environment. Synchrotron XRD techniques were used to monitor the phase transformations over time. The reacted products were further characterized by TEM. The study showed a complete conversion from ferrihydrite into magnetite within 30 hours at 20mM ferrous ion injection without any intermediate phase being detected. When injected with 2mM ferrous ion solution, magnetite was still the only secondary mineral phase detected, although the transformation took 150 hours to complete. Instead of a constant rate, the transformation reactions at the two conditions studied both showed slow rates at the beginning, but increased rapidly thereafter following a power rate law. The transformation rates obtained in this study are faster compared to the values obtained in traditional bench reactors experiments. The overall fast transformation process indicates a topotactic structure rearrangement resulting from electron transfer between injected ferrous ion and ferrihydrite without any significant dissolution and recrystallization. The transformation process conforms to a solid state transformation mechanism.

Mineral chemistry of carp otoliths reflecting water quality change

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The chemistry of fish otoliths is derived directly from their living environment, and once deposited the elements will be fixed forever. Therefore, analysing the mineral chemistry of otoliths is useful in the chemical evaluation of waters where the fish lived [1]. Our research reveals that the mineral chemistry of otoliths is a potential proxy for monitoring water quality change. Samples of carp and lake water were collected from Baiyangdian Lake, suffering from serious intermittent pollution, and Miyun Reservoir, supplying drink water for Beijing, which is little polluted. Both of these waters are located in northern China. The minerals within otoliths from both sites were vaterites. Trace elements As, Ba, Cr, Pb, Zn in the water samples were analyzed separately on AFS and ICP-MS. The contents of the elements in the water samples from the Baiyangdian Lake are all higher than those from Miyun Reservoir. Contents of all elements but Ba in otoliths from Baiyangdian Lake are higher than those from the Reservoir. These trace elements within lapillus were also measured on LA-ICPMS. The otoliths from the Baiyangdian Lake show higher concentrations of trace elements during winter to next spring and lower in the summer and autumn. This result is due to the discharging of waste water from the local factories during the winter to next spring, and replenishment from the upriver reservoirs by the government in the summer and autumn to prevent the lake from drying up and also to attract people for sightseeing. Otoliths from the Miyun Reservoir also show interesting records with quite high levels of As, Ba, Cr, Pb and Zn before the year 2003, but levels of nearly zero afterwards. This finding is consistent with strict water quality protection instigated by the city government.

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Superimposed processes of Gold and Silver mineralization in the Dayingezhuang gold deposit, Jiaodong gold province, China: Constraint of ore-forming fluid geochemistry

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The Dayingezhuang gold deposit is located in the central part of the Zhaoping Fault Zone, which is one of the most important gold-hosting faults in the Jiaodong gold province of China. Dayingezhuang is a typical large scale shear zone-hosted disseminated gold deposit with superimposed silver mineralization. Microthermometry of Fluid inclusion (FI) shows multiple values, indicating multi-stage hydrothermal fluid activities and mineralizing events. In general, ore-forming fluids are characterized by low salinity and low density. Homogenization pressures of FI are estimated from 20×10^5 Pa to 220×10^5 Pa. Redox conditions shifted from weak oxidation, through reduction, to weak reduction; and pH values varied from weakly acidic, through basic, to weakly acidic during ore-forming processes. Reduction and oxidation of silver mineralizing fluids are lower than those of the gold-bearing fluids. Gold mineralizing fluids are NaCl type and silver mineralizing fluids are rich in F. The change in ore-forming fluids from K_2SO_4 type to NaCl type indicates the superposition of two hydrothermal mineralizing events. Ore-forming fluids were dominated by magmatic components in early mineralization period, and affected by meteoric waters in late period. Gold may have been transported as Au-S or Au-Cl complexes, whereas silver was transported as Ag-Cl complexes. Early fluid boiling and later fluid mixing are thought to be two of the main factors causing the deposition and superimposing of gold and silver to form the large deposit.

Study of the rhizofiltration by using *Phaseolus vulgaris var.*, *Brassica juncea (L.) Czern.*, *Helianthus annuus L.* to remove Cesium from groundwater

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Rhizofiltration is one of the clean up processes by using plants (mainly their roots) to remove heavy metal from water.

Batch scale experiments were performed to investigate the cesium removal efficiencies of the rhizofiltration from the artificially contaminated groundwater having cesium concentration of 55.7 $\mu\text{g/L}$. Three terrestrial plants such as *Phaseolus vulgaris var.* (Bean), *Brassica juncea (L.) Czern.* (Indian mustard), and *Helianthus annuus L.* (Sunflower) were used for the experiment. The glass tank (12 cm \times 12 cm \times 8 cm) containing 400 ml of the artificially cesium contaminated groundwater was used as the growth chamber for the rhizofiltration. Groundwater in the growth tank was sampled at 12, 24, 48, and 72 hr and its cesium concentration was analyzed on ICP/MS (Perkin elmer, Elan6100(USA)). From the results of experiment, three plant cultivars reduced cesium concentrations from 55.7 to 0.3 $\mu\text{g/L}$ in groundwater within 12 h of rhizofiltration. After 72 h, its cesium concentration maintained at 0.013 $\mu\text{g/L}$ and the removal efficiency was 99.9 %. From the results of the analysis on the cesium accumulation for *Helianthus annuus L.* and *Phaseolus vulgaris var.*, 96 and 92 % of initial cesium were accumulated in the root and 4 and 8 % of cesium existed in the shoot part (including leaves), respectively. The amount of cesium transported to the shoot from the root for the rhizofiltration process was very small. To identify the effect of different cesium concentrations on the velocity and the magnitude of cesium removal from groundwater, three different plant cultivars were exposed to 400 ml of artificially contaminated groundwater with different initial cesium concentrations ranging from 150 to 500 $\mu\text{g/L}$ for 72 h. For *Helianthus annuus L.* and *Phaseolus vulgaris var.*, more than 99 % of initial cesium concentration were removed from the solution (500 $\mu\text{g/L}$) and the cesium concentration of residual solution maintained lower than 1 $\mu\text{g/L}$. For *Brassica juncea (L.) Czern.* with 500 $\mu\text{g/L}$ solution, the removal efficiency maintained about 60 % and was less effective, compared with those of *Helianthus annuus L.* and *Phaseolus vulgaris var.*

Sr-Nd-Pb isotopic systematics and the sediment source-to-sink pattern of the Changjiang (Yangtze) River

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The suspended particulate and fine-grained floodplain sediments were collected from the main stream and tributaries of the Changjiang River for Sr-Nd-Pb isotopic measurements. The $\epsilon_{Nd}(0)$ values gradually decrease downstream from -10.8 on average in the upper reaches to -12.3 in the lower reaches, whereas the $^{87}Sr/^{86}Sr$ ratios increase correspondingly, averaging 0.721899 and 0.725826 respectively in the upper and middle-lower reaches [1]. The Pb isotopic ratios show larger variations in the main tributaries, especially in the upper reaches, than those in the main stream.

The compositional variations primarily reflect the complex controls of provenance rocks, chemical weathering, and sediment characters between different catchments. The abnormal Sr-Nd isotopic compositions of the Yalongjiang, Fujiang, Tuojiang and Yuanjiang Rivers indicate the sediment provenance contributions from the Emeishan Basalt in the upper reaches and the old metamorphic and siliceous rocks in the middle-lower reaches. The Sr-Nd isotopic ratios of the Changjiang sediments can better reflect the average composition of weathered continental crust compared to other major rivers in the world because of the unique source rock types in the Changjiang drainage basin [2-5]. The recognition of the Sr-Nd-Pb isotopic systematics of the Changjiang sediments will contribute to our understanding of the Changjiang evolution history and continental weathering processes during the Cenozoic, and also to reconstruct the paleoenvironmental changes in East China and the marginal seas.

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Abnormally enriched arc lavas at arc-continent collision zone: An example from Lutao volcanics, offshore SE Taiwan

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The Taiwan-Luzon arc, which was generated in response to the subduction of the South China Sea, collided with the eastern margin of the Eurasian plate at the arc's southern and northern ends. As a consequence, volcanism ceased or was reduced to low levels in the proximity of the collision zones. Sr-Nd-Pb isotopic analysis indicates that the magma characteristics of the northern Taiwan-Luzon arc are strongly controlled by the heterogeneity of the mantle source ($^{87}Sr/^{86}Sr=0.70321\sim0.70569$; $\epsilon_{Nd}=+9.4\sim-5.8$; $^{206}Pb/^{204}Pb=18.13\sim18.54$) which produces extreme geochemical variations ($[La]_N=0.19\sim534$; $[La/Yb]_N=0.53\sim75.8$). The most enriched lavas occurred at Lutao volcanic islet, offshore of Se Taiwan, ca. 0.54-0.95 Ma. In general, the geochemical characteristics of the lavas changed dramatically 5-4 Ma ago. Temporal geochemical variations of the representative lavas from Taiwan-Luzon arc show that enrichment occurred in this area after 5 Ma. All of the younger lavas exhibit enriched geochemical signatures, i.e., high K_{Si} , LILE, $[La/Yb]_N$, and higher $^{87}Sr/^{86}Sr$ and low ϵ_{Nd} values. Various enrichment components have been proposed to account for the geochemical features of the Luzon arc lavas. Obviously, none of a simple two end-member, i.e., depleted mantle source and enriched component, mixing model can easily explain the systematic enriched characteristics of the arc magmas. Multiple source components and enrichment processes are necessary for the Taiwan-Luzon arc system. We consider that the continent-derived sediments shall play an important role in the magmagenesis during and after the arc-continent collision at both ends of the arc. Except for some of the unusual 'low-Nd' array, i.e., the lavas have Nd isotopic ratios below the so-called 'mantle array' in the Sr-Nd isotopic plot, all of the northern Taiwan-Luzon arc magma compositions can be explained by the subducted sediment and depleted mantle mixing model. Meanwhile, the 'low-Nd' array lavas, which mainly occurred around Lutao after 2 m.y. ago, may be the result of recently additional mixing of the enriched components which were lower crust melts for Lutao magmas.

Occurrence of Uranium minerals from sandstone-type Uranium deposits, Ordos Basin

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Introduction

The breakthrough of sandstone-type uranium deposits in Ordos basin, northern China in recent years marks the great achievement in Chinese nuclear exploration. Sandstone-type uranium deposit is one of uranium deposits with important industrial value, which is regarded as one of the main target exploration in Chinese nuclear geology.

Results

We had reported the ore-forming condition in sandstone-type uranium deposits [1, 2] and their geochemical characteristics [3] in Ordos basin. This study focuses on occurrence of uranium minerals in these sandstone-type uranium deposits with high-resolution of SEM and EPMA. The results show that most of the uranium minerals are in micro-grained distributed in potassic feldspar, microcline, quartz, muscovite and cement in the form of very tiny grains (<1 μ m). The contents of UO₂ are ranging from 0 to several percentage. Generally, the high-U bearing minerals are also containing high-Th and REE in the rocks. This study is of significance to both understanding of uranium enriching processing as well as utilization and metallurgic technology of U resources in sedimentary basin.

This study is supported by a 973 Key Project from Chinese Ministry of Science and Technology (2003CB214600).

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Rn concentration and estimation of annual effective dose in Xiazhuang Uranium Ore Field, Guangdong Province

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Xiazhuang granite-type uranium ore field is located in Ongyuan county, Guangdong province. In order to understand the radioactive environmental background in this area, the Rn concentration in soil was measured in field with FD-3017 RaA instrument. The result showed that average radon concentration in soil was 2019.42 Bq·m⁻³, in range of 35-70000 Bq·m⁻³.

And the radon concentration in the air 1m above ground surface was calculated using the earth-atmosphere radon exchange model.

$$C = \frac{\frac{A}{\lambda\eta} \cdot (\sqrt{v_1^2 + 4\lambda D_1} \eta - v_1)}{\sqrt{v_1^2 + 4\lambda D_1} \eta + v_1 + \sqrt{v_2^2 + 4\lambda D_2} - v_2} \cdot \exp\left(\frac{\sqrt{v_2^2 + 4\lambda D_2} + v_2}{2D_2} \cdot X\right)$$

In the formula:

A=2.64×10⁻⁴· ρ ·w(U)·Kp· α ;

C is Rn concentration in air (Bq·m⁻³);

D₁ and v₁ are diffusion coefficient (cm²/s) or convection speed (cm/s) of radon in rock or soil, respectively;

D₂ and v₂ are diffusion coefficient (cm²/s) or convection speed (cm/s) of radon in air, respectively;

ρ is density of rock or soil (g/cm³);

w(U) is uranium concentration in rock or soil (%);

λ is decay coefficient of radon (s⁻¹);

Kp is balance coefficient between uranium and radium;

α is emanation coefficient of rock or soil;

η is porosity of rock or soil;

X is the height between ground surface and measuring point (cm).

The research indicated that, the mean values of radon concentration in air was 56.21 Bq·m⁻³, in range of 26.98-167.67 Bq·m⁻³. The annual effective dose caused by radon was 3.81mSv, about 3 times higher than that in our country which is 0.88 mSv.

This study was granted by the National Natural Sciences Foundation of China (Grant No. 40774075).

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Geochemistry of Silicon and Oxygen in the regolith on Feihong Ultramafic Complex, West Yunnan, China

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The regolith on Feihong ultramafic complex, approximately 20km southwest of Luxi in western Yunnan, can be divided into five horizons (Fig. 1).

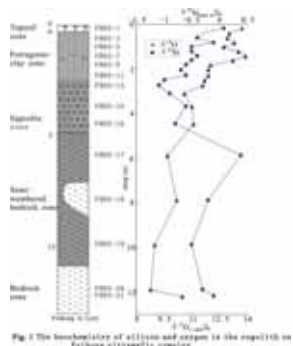


Fig. 1 The number of silicon and oxygen in the regolith on Feihong ultramafic complex.

The authors tested samples from every horizon and got the dates of $\delta^{30}\text{Si}_{\text{NBS-28}}$ and $\delta^{18}\text{O}_{\text{V-SMOW}}$. Fig.1 illustrates from the bedrock zone to the topsoil zone the values of $\delta^{18}\text{O}_{\text{V-SMOW}}$ give a rising trend but the largest value plots at Ferruginous-clay zone. The values of $\delta^{30}\text{Si}_{\text{NBS-28}}$ can be divided into two groups. The first group includes the dates in semi-weathered bedrock zone and bedrock zone and the rest is another group. The values in the first group are higher than the second group and in the second group from saprolite zone to topsoil zone the values of $\delta^{30}\text{Si}_{\text{NBS-28}}$ give a rising trend.

Based on the composition of every zone [1] we can see that along with the increasing weathered degree the values of $\delta^{18}\text{O}_{\text{V-SMOW}}$ become large and large. Because in the Ferruginous-clay zone the clay minerals are mainly goethites [1] whose $\delta^{18}\text{O}_{\text{V-SMOW}}$ are large, the largest value plots at this zone. The values of $\delta^{30}\text{Si}_{\text{NBS-28}}$ in the semi-weathered bedrock zone and bedrock zone are larger than the other four weathered zones. Meanwhile by the leaching and desilication in the saprolite zone and Ferruginous-clay zone, the silicon transport downwards. When they reached saprolite zone which represents the ground-water level the silicon accumulate here and the values of $\delta^{30}\text{Si}_{\text{NBS-28}}$ reach the least.

This study indicates the geochemistry of silicon and oxygen can reflect the degree of weather. While the $\delta^{18}\text{O}_{\text{V-SMOW}}$ is large, the rocks are weathered more. The values of $\delta^{30}\text{Si}_{\text{NBS-28}}$ become larger while rocks are weathered and they can reflect the location of the ground-water level.

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Metallogenic controlling factors for metamorphic-sedimentary Mn-deposits in Hougou-Dapingshan Area, South Qinling Orogenic belt

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Introduction

We recently founded the Hougou-Dapingshan manganese (Mn) and phosphor (P) metallogenic belts including three high quality metamorphic-sedimentary Mn deposits. This belt is located in the middle-east part of the South Qinling Mn-P metallogenic zone. The three high quality Mn ore-bodies are carbonaceous argillaceous rock-carbonatite formations of Tananpo Formation (Lower Cambrian) which belongs to Mn-bearing facies by function of metamorphism. This Mn-P metallogenic zone is a potential non-metal mineral resource base in China.

Results

Based on the Mn metallogenic and geological characteristics, we discussed the metallogenic condition of high quality Mn deposits. The results indicate that the Mn-bearing sediments were controlled by fissured depressive tectonic basin, i.e. crystal basement, whose characteristics is the transitional crust property of Pre-Sinian System (later Proterozoic). The metallogenic geochemical background indicates Mn and P concomitance, lower Co content, lower Co/Ni ratio and Ni, Cu, Pb, Zn and B of higher coefficient of enrichment and polygenous metallogenic compositions. Mn metallogenic process has evident feature of basin-controlling, schistosity-controlling, single lithology. High quality Mn ore are controlled by Mn-P-bearing sedimentary rocks and Mn metallogenic seam exists on the P metallogenic seam. Manganic limestone (including dolomite limestone) and pyritic cherty schist are considered as prospecting indications.

This study is supported by the Chinese Ministry of Science and Technology (2003CB214600).

Diversity and vertical distribution of cultured SRB in an intertidal bog of the coastal mangrove from Hainan island

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In the Eastern Hainan province, the mangrove bog (modern to 10,000 years) are strongly affected by tidal fluctuations, and contain anoxic environments where sulfate reduction is an important microbial metabolic process. The objective of this study was to characterize the sulfate-reducing bacteria community in the profiles of the mangrove peat based on a phylogenetic analysis of sulfate-reducing bacteria.

There are several tens species of main advantage germ (SRB) clusters above 80cm in the depth profile of the bog sample. With the burial depth increasing, generally, the species and the cell number decrease. The results can be explained by the long periods of flooding to which these substrates are subjected every day which cause, different redox conditions in the subsurface and surface layers. But there exist high concentrations of cells correlated positively with the pyrite-sulfur, which belong to the boundary between the pedogenesis and the diagenesis of mangrove bog (Fig. 1. the highlight data points, approximately depth 30cm). This layer contains relatively stable redox condition, giving rise to the formation of polysulphides that allow rapid formation of pyrite.

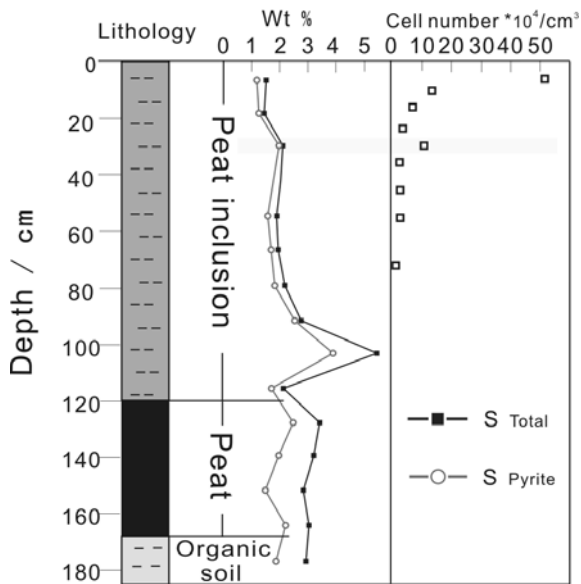


Figure 1: Depth profiles of the S values and cell (SRB) number in the mangrove bog from Hainan island.

Sedimentary brines in ore deposits and basement rocks

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A wide range of low temperature Pb-Zn deposits, including both sediment-hosted and basement-hosted examples, have formed from saline fluids which are close to salt-saturation at surface temperatures (equivalent salinities c.21 - 24% NaCl). Similar fluids are also found in basement rocks without mineralisation, and likewise are bittern brines with Br:Cl ratios greater than seawater. The frequent occurrence of brines of this salinity suggests an origin at the surface, where they would be close to salt-saturation. Such bittern brines have a higher geological preservation potential than their associated evaporites. In addition to Br-enrichment, they commonly show evidence for extensive fluid-rock interaction with elevated levels of Ca and transition metals relative to evaporated seawater.

Brines formed in the sub-surface may be more saline, reflecting the higher temperature at which salt-saturation was attained. Those produced by dehydration of crustal fluids due to the growth of hydrous minerals have a wide spectrum of salinities up to a maximum corresponding to local salt saturation.

Brines formed by dissolution of halite are known from sedimentary and low grade metamorphic settings, and in addition to lower Br:Cl ratios, they typically have very high Na:Ca because the Na-content of the pore water exceeds the available Ca from mineral alteration. Such brines have the potential to equilibrate with rocks and play a role in metal transport, but are normally low in most metals other than Na.

We conclude that, directly or indirectly, surface evaporation is the principal process leading to the development of saline fluids in the crust and is the primary control on many types of ore body.

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The Helium and Neon isotopic compositions in the Beimarang ophiolites from the Yarlung Zangbo River, Tibet, SW China

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The noble gases isotopic compositions in the Beimarang ophiolites from the Yarlung Zangbo River, Tibet, SW China were measured by MM5400 mass spectrometer using stepwise heating method. A large amount of He was released at 700°C for serpentinite and a altered pyroxene peridotite, and at 300°C for the others. The temperature released maximal He contents was decreased with the increased altered grade. The R (³He/⁴He) value in the serpentinite was 7.02Ra (Ra = 1.400×10⁻⁶, is the ³He/⁴He ratio in air), 4.63Ra, 5.81Ra and 4.56Ra, at 300, 700, 1100, 1600°C, respectively. The R values in the altered pyroxenic peridotite were between 0.389Ra and 1.72Ra at various temperatures. The R value in a hornblende diorite was also 1.16Ra at 1100°C. Considering metamorphism, it is supposed that the R value of the original fluid in the serpentinite would be higher than 8Ra, which is the typical value in MORB. The peridotite, the matrix of the serpentinite, maybe comes from lower mantle. For the two altered hornblende diorites, the R value was decreased with the increased altered grade. In these samples, the ²⁰Ne/²²Ne ratios were between 10.6 and 16.18 with an average of 12.49, and the ²¹Ne/²²Ne values were between 0.02789 and 0.062 with an average of 0.03665. The data points of the samples were mainly arrayed along L-K (Loihi-Kilauea, hotspot) line in the three isotopic diagram of the neon. Summarily, the obtained data indicate that the formation of the Neo-Tethys Ocean, which was represented by the Yarlung Zangbo River ophiolites, would be associated with a plume-type volcanism.

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Isotopic and elemental constraints on the first 100 Myr of Earth history

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James Hutton (1785) in formulating his concept of *Deep Time* stated there is "...no vestige of a beginning, no prospect of an end" for the Earth. Emerging evidence at the dawn of the 21st century from radiogenic daughter isotopes of short-lived, now extinct radioactivities, suggests that every single piece of rock one could pick up on the Earth's surface faithfully records the vestiges of a beginning, no matter how effective the Earth was in concealing its early history. It is often stated that there is no rock record from the Hadean era, the first 500 Myr of the Earth history. However, modern isotope geochemistry shows that all rock samples we can lay our hands on have acquired their chemical and isotopic characteristics from the Earth's first 100 Myr, even as early as the first 10-30 Myr history after the Solar System's birth.

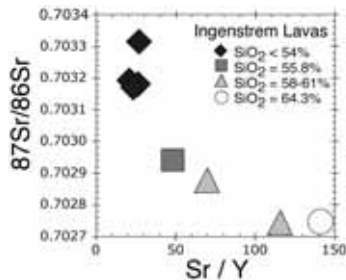
The current prevailing paradigm for the last stage of planet formation is characterised by 20 or so Mars-sized planetary embryos perturbing each other into crossing orbits and merging into the present configuration of four inner planets via giant impacts. Our satellite Moon is thought to be a by-product of the last giant impact on Earth. We thus resort to the Moon for additional information for the first 100 Myr of Earth history. The W isotopic composition of the Moon has evolved through four iterations in the last decade (1997, 2002, 2005, 2007) in the geochemists' ongoing quest for the truth. It is now added to the group of elements (e.g. O and Cr) that show a remarkable similarity in their isotopic composition between the Earth and Moon. However, such similarity does not imply that the Earth-Moon system was formed after ¹⁸²Hf had decayed (>60Myr), as incorrectly stated in the recent literature. Still the bulk silicate Earth and the Moon are radiogenic by 2 epsilon units (ϵ_{182W}), reflecting their ingrowth from high Hf/W reservoirs when ¹⁸²Hf was extant. The "flat isochron" of high-Ti, low-Ti and KREEP basalts only reflects later internal silicate differentiation within the Moon. This information is not directly relevant to the timing of Moon formation, as we cannot argue Earth is ~4 Gyr old using Acasta gneiss. The key question is *are Hf/W ratios for the bulk silicate Earth and Moon distinguishable?* If the Moon is made from the Earth mantle material due to the giant impact, thus having similar W isotopic composition, logically their bulk Hf/W ratio should be the same. As neither Hf nor W are volatile, significant fractionation between them is unlikely during the Moon formation event.

Western Aleutian and Kamchatka high-Mg# Andesite and Dacite

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Recent mapping has identified an active field of high-Mg# andesite/dacite volcanism on the western Aleutian seafloor in the area of the Ingenstrem Depression, a rectangular basin that lies on the Aleutian Ridge crest west of Buldir island, the western-most emergent volcano in the arc. Ingenstrem lavas include a large proportion of primitive samples ($Mg\# > 0.60$) which span the basalt-dacite compositional range (50-67% SiO_2). Basalts have moderately enriched trace element patterns ($La/Yb=4-8$, $Sr/Y < 30$) and relatively radiogenic Sr compared to MORB ($^{87/86}Sr=0.7031-0.7033$). In contrast, high-Mg# andesites and dacites have high Sr (700-2300 ppm) and fractionated trace element patterns ($Sr/Y > 50$), with low Y (<12 ppm) and HREE's. Samples with high Sr/Y also have systematically higher SiO_2 , Mg#, Cr and Ni. Ingenstrem lavas of all compositions have Sr isotopes that are inversely correlated with Sr/Y and SiO_2 , so the most felsic samples (66-67% SiO_2) have the most fractionated trace element patterns ($Sr/Y > 120$) and the least radiogenic Sr ($^{87/86}Sr < 0.7028$; see figure). Pb isotopes indicate that the Ingenstrem lavas contain little subducted sediment ($^{206/204}Pb=18.41-18.56$), but the narrow range for Nd isotopes ($\epsilon Nd=8.5-9.5$ with $^{87/86}Sr=0.7027-0.7033$) suggests that there may be an important source component for these rocks in seawater-altered oceanic crust. Ingenstrem andesites and dacites are crystal-rich, with phenocrysts of plagioclase, pyroxene and amphibole. In this way they contrast primitive andesites from the Shisheisky Complex, a field of monogenetic cones north of Shiveluch Volcano in Kamchatka [1], which have higher MgO (~8%), are aphyric or olivine phyric and lack phenocrysts of plagioclase.



Textural, mineralogical and major element differences between these primitive andesite suites probably reflect a key role for pre-eruptive volatile loss, which drove late crystallization to produce the phenocryst-rich textures and slightly fractionated compositions of the Ingenstrem compared to Shisheisky lavas.

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Geochemistry of coordination space on the surface of manganese dioxide covered with hydroxyl groups

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Introduction

Manganese crust consisting of manganese dioxide (MnO_2) in marine environment concentrates platinum (Pt), that is, the Pt content of manganese crust is higher compared with that in Earth crust. On the other hand, the gold (Au) content of manganese crust is lower than that in Earth crust. This different behavior for Pt and Au is one of the most attracted problems in geochemistry. The contents of Pt and Au are considered to be controlled by adsorption on MnO_2 . In this study, therefore, adsorption behavior of Pt(II) and Au(III) complex ions on MnO_2 was investigated in order to elucidate the difference in geochemical behavior of Pt and Au in marine environment.

Results and Discussion

Behavior of Pt(II)

In the pH range 4 – 6, the amount of Pt(II) adsorbed on MnO_2 increased with increasing pH and the amount attained a constant value above pH 6. As the PZC (point of zero charge) of MnO_2 is around pH 4, Pt(II) was considered to be adsorbed by the specific adsorption. From XPS spectra for Pt adsorbed on MnO_2 and its EXAFS analysis, the adsorbed 4-coordinated Pt(II) with square plane structure was oxidized to 6-coordinated Pt(IV) with octahedral structure by Mn(IV) in MnO_2 . The coordinated atoms for the Pt(IV) were all oxygen atoms, indicating that the Pt(IV) was substituted to Mn(IV) in MnO_2 by isomorphous substitution. The concentration of Pt in manganese crust is concluded to be caused by the oxidative substitution

Behavior of Au(III)

In the pH range 4 – 6, the amount of Au(III) adsorbed on MnO_2 increased with increasing pH and the maximum amount appeared at pH 6. Au(III) was also adsorbed by specific adsorption. However, a part of Au(III) adsorbed was reduced to atomic gold, Au(0), even in the absence of specific reducing reagents. The Au(0) is probably desorbed from the surface of MnO_2 . Accordingly, concentration of Au into manganese crust hardly occur.

Osmium partitioning behavior between metal and silicate melt at high pressure and temperature: A new experimental approach

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Constraining partitioning behavior of the highly siderophile elements (Re, Os, Ir, Ru, Rh, Pt, Pd, Au: $D_{\text{met/sil}}^{\text{met/sil}} > 10^4$ at 1 atm) may play a key role in elucidating whether mantle abundances of these elements were established by metal-silicate partitioning at the base of a magma ocean, or by accretion of ~0.5% of Earth's mass subsequent to core segregation. Osmium is an important element in discriminating between these processes, owing to the utility of the ^{187}Re - ^{187}Os isotope system. Yet data for $D_{\text{Os}}^{\text{met/sil}}$ for high P - T conditions are generally lacking. We have devised a new methodology to determine $D_{\text{Os}}^{\text{met/sil}}$ at high P - T conditions while utilizing natural Os abundances in the experiments. Paired samples of iron meteorite ($^{187}\text{Os}/^{188}\text{Os} = 0.14$; Os = 8.5 ppm) and komatiitic basalt ($^{187}\text{Os}/^{188}\text{Os} = 2.2$; Os = 64 ppt) are placed in graphite capsules and processed at 10 kbar–1450°C or 20 kbar–2000°C. The $^{187}\text{Os}/^{188}\text{Os}$ and Os concentrations in several small (<10 mg) portions of quenched glass from each experimental charge are measured by physical separation, chemical separation of Os from the glass and analysis of Os by negative thermal ionization mass spectrometry. The data for 10 kbar–1450°C experiments show variable $^{187}\text{Os}/^{188}\text{Os}$ ratios (0.14–2.1) which span the range defined by the starting metal and silicate. The data show linear correlations in $^{187}\text{Os}/^{188}\text{Os}$ vs. $1/^{188}\text{Os}$ diagrams that converge at one end at the composition of the starting metal, suggesting variable contribution of metal micronuggets entrained in silicate glass. The other end-component has a $^{187}\text{Os}/^{188}\text{Os}$ ratio close to that of the starting silicate, but with an Os concentration that is lower than the starting silicate (43 ppt). This is likely caused by a draw down of Os from the silicate into the metal micronuggets, albeit without accompanying isotopic exchange. In the 20 kbar–2000°C experiments, the quenched glass retains Os concentrations lower than the starting silicate (<30 ppt) but have much lower $^{187}\text{Os}/^{188}\text{Os}$ ratios (<0.4) suggesting that isotopic exchange is more rapid at higher P - T conditions. Our experimental data give $D_{\text{Os}}^{\text{met/sil}} > 3 \times 10^5$, similar to prior 1 atm experiments ($D_{\text{Os}}^{\text{met/sil}} = 10^6$).

Experimental investigation of the hydrothermal geochemistry of Gold deposition associated with aluminosilicate: The formation process of epithermal Gold deposits

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In order to discuss the formation mechanism of epithermal gold deposits, synthetic experiment of aluminosilicate containing gold at 30°C and high temperature (<250°C) is demonstrated. As a preliminary experiment, coprecipitation of gold with aluminum hydroxide is investigated at 30°C. The gold complex, $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ is selected as model gold species in solution for convenience. The results show that the amount of gold coprecipitated with aluminum hydroxide decreased with increasing pH. Uptake of gold by aluminum hydroxide effectively occurred at near neutral pH, while almost no uptake by silicate. This result indicates that the electrostatic force between gold complex ions with three negative charges and aluminum hydroxide or silicate is the main factor for controlling the uptake of gold. The gold coprecipitation by aluminum hydroxide in the presence of various concentration of silicate is also examined. The amount of gold coprecipitated was affected toward decrease by addition of silicate. The detail investigation has to be done by NMR to discuss more in terms of coordination environment of aluminum or silicon with or without gold.

Since a boiling is recognized as a one of the key factor for the precipitation of gold associated with silicate from the ore-forming fluid, the model experiment at high temperature is designed. The sample solution containing gold, aluminum and silicon with a given concentration is prepared in a reactor. The reactor is constantly agitated and heated with monitoring temperature and pressure. At designed temperature, the valve is opened and the makes the sample solution boiled as a function of the decompression rate. The obtained product of solid material is characterized by XPS, XRD, NMR and SEM/EDX to discuss the relationship between change in chemical state of gold and distribution of other elements. The formation mechanism of epithermal gold deposit will be proposed based on the obtained results.

Some innovative measurements and analyses of isotopically substituted molecules of geochemical interests

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Isotopes have been used to trace the origin of materials and their cycles in geochemistry and cosmochemistry. Researches have been developing from single isotope analysis to multiple isotopes tracer analysis. Recent innovations in measurement have opened the frontier of the isotopomer analysis. The term isotopomer is used to involve any components arising from isotope substitution of materials including present IUPAC narrow definition of isotopically substituted isomer. Non mass dependent isotope fractionation (NMD-IF) of oxygen and sulfur containing molecules such as SO₂, multiple heavier isotopes substituted molecules such as mass 47 CO₂, and the preferential isotope substitution of different positions in a molecule species such as O₂ and N₂O are those representatives.

We have developed several measurement technologies, applied them to some molecules of geochemical interests, opened the methods, synthesized standards, and discussed wide open in the International Symposia on Isotopomers (<http://nylab.chemenv.titech.ac.jp/isi.html>). Some recent innovations in isotopomer measurements are briefly summarized, their applications to OCS, SO₂, CO₂, N₂O and some organic molecules are described, and their implications and the future perspectives will be discussed.

Rb-Sr isotopic systematics of two-pyroxenes and olivines from dunite channels, the Horoman peridotite complex, Japan

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The Horoman peridotite complex is one of the freshest orogenic peridotite complexes in the world. Dunite channels occur as dykes of both large scale (several 10 meters width) concordant layers [1] and small scale (< several meters width) discordant layers [2]. The small scale dunite channels incorporate two-pyroxenes + spinel segregations and are interpreted as replacement in origin [2, 3]. In this work, we present the Rb-Sr isotopic compositions of olivine, orthopyroxene and clinopyroxene from dunite dyke swarm sample (Nos. SPR4 and 6) and the wall harzburgite (No. SPR14).

The data obtained and the previously reported [4] indicate that the orthopyroxenes and clinopyroxenes from both the channels and the wall harzburgite have reached equilibrium at a subsolidus-condition, or that the migrating melt was originated from the identical wall harzburgite. This melt-channelling event could generate around 50 Ma, coeval with that of the peak metamorphism of surrounding Hidaka metamorphic rocks. On the other hand, olivines from the SPR 4 and SPR14 are not plotted on the clinopyroxenes-orthopyroxenes line of the ⁸⁷Rb/⁸⁶Sr-⁸⁷Sr/⁸⁶Sr diagram. These findings lead to the inference that the olivines were re-equilibrated by later thermal event, because of their higher diffusion coefficient.

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The effect of aspartic acid on dissolution of calcite

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Interactions between some amino acids and crystals of calcium carbonate have been investigated to elucidate the biomineralization mechanism. Among amino acids, aspartic acid (Asp) particularly draws attention because, during the process of biomineralization, some Asp-rich peptides are known to control the polymorphism and structure of calcium carbonate. The present study aimed to clarify the effect of Asp on the dissolution of calcite from measurements of dissolution rate and surface morphology.

The dissolution rates were determined directly from $[Ca^{2+}]$ increasing with calcite dissolution reaction in Asp 0–0.1 M aqueous solutions. Initial condition of reaction solution was adjusted to pH = 8 and ionic strength = 0.1 M using NaOH, HCl, and NaCl. The obtained dissolution rate indicated that Asp inhibited the surface reaction process and accelerated the transport process in calcite dissolution. The crossover of these contrastive effects caused the transition of rate-determining processes of calcite dissolution.

AFM observations of calcite surface in Asp 0–0.1 M aqueous solutions were performed in an AFM flow-through cell. Dissolution rate of calcite was also determined simultaneously from the difference of $[Ca^{2+}]$ between the input and output solutions. The pH of input solution was adjusted to 8 using NaOH and HCl. With increasing [Asp] the obtained dissolution rate increased for [Asp] lower than 0.03 M and decreased for [Asp] higher than 0.03 M. AFM observation revealed that etch-pit density on cleaved surface of calcite increased with [Asp] up to the concentration of 0.03 M. This result is consistent with the [Asp] dependence on the dissolution rate. In addition, we observed not only triangular etch-pit, which was reported by Teng and Dove (1997), but also pentagonal etch-pit in the condition of [Asp] = 0.03–0.07 M. Our study suggests that this morphological change derived from stabilization of [010] step caused by Asp.

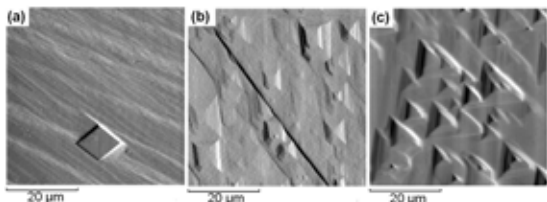


Figure 1: AFM images of cleaved surface of calcite taken at an hour later from starting of dissolution: (a) Asp-free (b) Asp 0.03 M (c) Asp 0.1 M.

Cenozoic alkaline and carbonitic magmatism in northeastern Tibetan Plateau: Implications for mantle plume

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The volcanic rocks of kamafugites and carbonatites outcropped geographically the range of E. 33°50'–34°15' in longitude and N. 104°15'–105°15' in latitude of Western Qinling, Gansu Province, and located in Tianshui-Lixian Cenozoic basin, North-eastern borderary of Tibetan plateau on the geotectonics. The extrusive carbonatites, specially emphasized, have strato-volcanoes and associated with tephra cones, tuff rings, diatremes and contemporaneous kamafugite lava or tuffs. The studies on the mineralogy, petrology show that there are those end members of potassic volcanic rocks, such as mafurite, ugandite, katungite, alnoite, aillikite and calcitite et al. The Ar/Ar isotopic dating for 6 individual phlogopites respectively demonstrate volcanic activity of the kamafugite and carbonatite in west Qinling occurred at Neogene (23Ma).

Both kamafugite and carbonatite are characterized by strong enrichment in incompatible trace elements and LREE. A variable but coherent initial $^{87}Sr/^{86}Sr$ (range is 0.70383–0.71336, mean $^{87}Sr/^{86}Sr$ is 0.70524 for kamafugite and 0.70934 for carbonatite), $^{143}Nd/^{144}Nd$ (range is 0.512221–0.512928, mean $^{143}Nd/^{144}Nd$ is 0.512794 for kamafugite and 0.51261 for carbonatite), and ϵNd (the range is of 1.3–5.58 for kamafugite and 2.4–5.7 for carbonatite), and Pb isotopic ratios (e.g. 18.149–22.4 for $^{206}Pb/^{204}Pb$, 15.476–15.727 for $^{207}Pb/^{204}Pb$, 37.613–39.33 for $^{208}Pb/^{204}Pb$ both kamafugite and carbonatite). The mean ratios of La/Nb, Ba/Nb, Ba/La, Zr/Nb and Sm/Nb are 0.84, 12.7, 15.6, 3.4 and 0.13 for kamafugite, and 1.04, 23.9, 23.6, 5.4 and 0.15 for carbonatite respectively. All of the data plotted respectively in the diagrams of ϵNd vs $^{87}Sr/^{86}Sr$, ϵNd vs Sm/Nb, Zr/Nb vs La/Nb and Ba/La vs Ba/Nb, and fell the area near the OIB and EM1 or EM11. For this reason mentioned above, we suggest that there are mixtures of the endmember composition at least two types of source materials. The geochemical characteristics of the OIB coupled with the geophysical information, temporal and spatial association with collision of Indian and Eurasian continents and strong uplift of Tibetan plateau, are thought to indicate that the WQL kamafugite and carbonatite magmatism formed as a consequence of asthenosphere upwelling pulled by plume.

[1] Yu XH *et al.* *Acta Petrologica Sinica* 17, 366–377. [2] Yu XH *et al.* *Science in China*(Series D) 44, 155–161.[3] Yu XH *et al.* *Acta Petrologica Sinica* 19, 105–112. [4] Yu XH *et al.* *Acta Petrologica Sinica* 20, 483–494.

Genesis of the native copper mineralisation in Eastern Tianshan

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Geological Characteristics

The native copper mineralization was discovered recently in the Eastern Tianshan of North Xinjiang [1]. The mineralization occurred in the Matoutan Group of Upper Carboniferous [2]. Native copper is the only metallic mineral. The native copper occurred in the alterative tuff in Shilipo area, in the basalt in Changchengshan and Heilongfeng area, and in the amygdaloid bodies of basalt in Dongjianfeng area. There are weak silication, epidotization, chloritization and zeolitization around the mineralisation bodies.

Discussion

The mineralisation type and minerogenetic system of the native copper mineralisation in the study area are different from those in Emeishan flood basalts, southwest China and the Keweenaw in America [3, 4], which may result from different genesis. According to the mineralization type, metallic mineral and alteration type, the genesis of the native copper mineralization may be controlled by the magma fractionation and syngenetic hydrothermal activation in Eastern Tianshan.

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Simultaneous determinations of U-Pb age, trace element compositions and Hf isotopes of zircon by LA-Q and MC-ICPMS

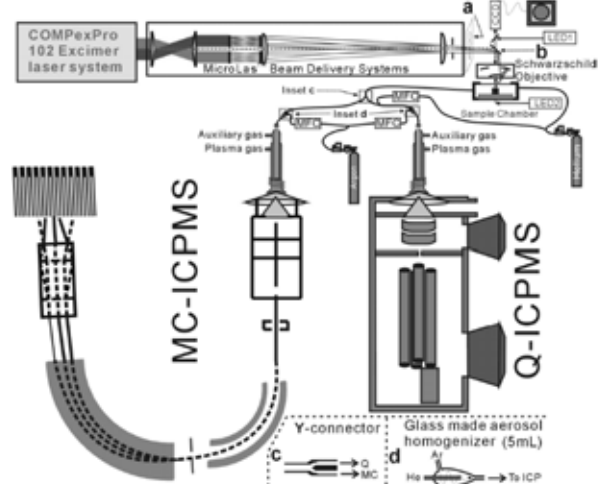
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A laser-generated zircon aerosol was split behind the ablation cell into two transport tubes via a Y-shaped connector and simultaneously introduced into the two mass spectrometers. Hafnium isotopes were measured on the MC-ICP-MS instrument, while U-Pb ages and trace element compositions were determined using the Q-ICP-MS.



For the 44 micron spot, the resulting U-Pb ages, Hf isotopic and rare earth element (REE) compositions of these six zircons agree with recommended/reported values within 2 σ error.

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[1] Yuan *et al.* (2008) *Chemical Geology* **247**(1-2), 100-118.

Apatite fission track constrains on the mineralization of Dashui Gold deposits, northern Qinghai-Tibet plateau

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Dashui gold ore district is located at southern foot of Xiqingshan Mountains, northern Tibet-Qinghai plateau. The gold deposit belongs to low-to-moderate temperature magmatic hydrothermal deposit.

The quartz diorite samples have apatite fission track ages (FTAs) of 132-189 Ma and average track length of 13.6 μm ; alteration quartz diorite are 135-156 Ma and 13.7 μm ; the ore samples are 107-168 Ma and 13.4 μm , and the breccia samples are 119-160 Ma and 13.1 μm . Thus, it can be seen that the quartz diorite has the highest fission track age, the ore takes second and the magmatic cryptoexplosion breccia is lowest.

It is known that there are $^{40}\text{Ar}/^{39}\text{Ar}$ plateau age of 222.5~235 Ma for the diorite. In view of much lower retention temperature of the apatite FTA than the that of $^{40}\text{Ar}/^{39}\text{Ar}$ age, the average FTA of 158 Ma for the quartz diorite and 140 Ma for the breccia basically accord with these isotopic ages. Meanwhile, because metallogenic temperature was 130-294°C in the ore district, we consider that these apatite FTAs could represent the ending time of the mineralization. The reason that the breccia has the lowest fission track age is that the cryptoexplosion breccia occurred in postmagmatic stage. The breccia intrusion could have resulted in a hydrothermal mineralization which overlapped the early stage of mineralization. It is that the magmatic breccia overlapping thermal event prolonged whole mineralization duration.

Effect of humic acid on absorption and partition of heavy metals for the Changjiang estuary sediment

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Organic matter in sediments varies significantly in the estuary region. It plays a major role in absorption and partition of metal pollutants for sediments.

Sediments were collected in the Changjiang estuary, which have low organic matter and heavy metals. The humic acid (HA) with 0%, 1%, 3%, 5% and 10% of sediment weight were mixed with sediments. Heavy metals added in the experiment depended on the half-death content of *Scallop* in 48 hours and the partition coefficients between water and sediment. The forms of heavy metals were determined by AAS with BCR sequence extraction method.

Results showed Cu and Pb increased rapidly from zero to 3% HA, and keep stably then in sediments. Zn and Cd increased slightly. The soluble fraction decreased and the oxidisable fraction increased for Cu, the reducible fraction increased evidently and the other three fractions decreased slightly for Pb. The reducible Zn increased and the residual fraction decreased slightly. The effect of humic acid on Cd was not significantly. So we think humic acid makes an obviously effect to Cu and Pb, but a trifling effect to Zn and Cd in sediments from the Changjiang estuary.

The partition of metal speciation is not only associated with organic acid, but also with the properties of heavy metals and the bound forms. The oxidisable form is dominant for Cu and Pb, and it has the strong combining ability with HA. Zn and Cd mainly exist in the soluble fraction and the residual fraction, they are not easy to integrate with HA. Otherwise, the different complicated modes between metals and HA (inner and external complication) also take an important function to impact on the bioavailability of heavy metals in the estuary sediment.

Source of sediments and metal fractionation in the swamp of two Chinese estuaries

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The Changjiang estuary and the Jiulongjiang estuary are located in east and southeast China, which belong to the meso-tidal type and the liman type respectively. Sources of sediments are associated with the circumstance around estuaries, which affect the total contents and speciation of heavy metals.

The major elements and heavy metals were analyzed by ICP-AES and AAS. SiO₂, CaO, MgO are higher in sediments from the swamp of Changjiang estuary, and Al₂O₃, Fe₂O₃, OM are higher in sediments from the Jiulongjiang estuary. Heavy metals in sediments of the swamp of Jiulongjiang estuary are higher than in those of the Changjiang estuary. Sediments in the Changjiang estuary have higher soluble Cd and Pb, reducible Cr, oxidisable Cu and Zn, those in the Jiulongjiang estuary have higher soluble and reducible Zn, oxidisable Cu, Pb and Cr.

The primary component analysis of major elements and heavy metals shows that Pb is associated with CaO, Cu is associated with Fe₂O₃, MnO and organic matter, and Zn, Cr, Pb are associated with Al₂O₃ in sediments of the Changjiang estuary. Zn, Cd, Pb are associated with CaO, Cu is associated with Fe₂O₃, Zn is associated with MnO, Cu and Zn are associated with organic matter, Cr is associated with Al₂O₃ in sediments of the Jiulongjiang estuary.

The sediments from the Jiulong swamp as a result of semi-closed bay mostly originate from the ambient soils with high contents of clay and organic matter, which can absorb the metal pollutants. But the Changjiang estuary is strongly affected by the riverine discharge, and sands from river deposit in sediments. The metal pollutants are diluted in the estuary swamp.

Mineralogical-geochemical peculiarities of sulfur-phosphate acidic weathering in arctic conditions

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For the last thirty years (1977-2007), black carbonaceous-argillaceous-siliceous shale hypergenesis processes in arctic conditions have been studied (Pai-Khoi, the Yugorsky Peninsula, Russia) and their comparative analysis with identical processes, developing in similar geological environments in arid climate conditions (Kazakhstan, Spain), has been carried out by us.

The main factor of hypergenic mineral formation is sulfur-phosphate acidic weathering. Freeze melt waters, infiltrated from loose covering deposits, influence on sulfide and phosphate containing black shales and are enriched by sulfuric, phosphoric and other acids, the concentration and activity of which increase sharply as a result of acid bath freezing in oxidizing rock outcrops. Fluid Si-Fe-Al-SO₃-P₂O₅ hydrosols, with the consistence from syrupy up to retinoid, are formed. They fall into two geochemical branches: aluminum and ferrous. Their coagulation leads to the formation of hard hydrogels and crystallization of Ca, Mg, Fe, Al, etc. sulfates. As a result of hydrogel salting-out under the influence of electrolytes, gypsum, jarosite, epsomite, and copiapite are crystallized, and also amorphous aluminophosphates are transformed into crystalline crandallite. The minerals of the system Si-Fe-Al-SO₃-P₂O₅ last evolution stage are wavellite, variscite, turquoise, etc.

The general mineral formation evolution consequence in the system of ageing colloids in Arctic is the same as in other regions, but evolution rows are much more complete because in arctic conditions, less stable short-lived phases, which in arid climate conditions immediately destroy, passing into more stable ones, are better preserved.

Ultra-high-speed electroatmogenic transformation of humus matter into naphthoid

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Fulgurites are a geological consequence of a lightning stroke to rocks. They are tubular or drop-shaped form composed of glass, relics of surrounding rocks and new mineral formations. Two types of fulgurites are noted. They are determined by target rocks: *clastofulgurites* (aleuro- or psammito-) formed on different porous rocks, and *petrofulgurites* resulted from lightning discharge on exposed hard rocks. We have discovered a new type of fulgurites – *phytofulgurites* which formed on plants. A lightning stroke to a dry haycock resulted in grass inflammation and its partial coking in the lower part without air access. On the ground among ash a cake-like body was found which had rolled fibrous structure. It was presented by a complex hydrocarbon polymer $C_{411}H_{182}N_{26}S$ corresponding to natural medium anthraxolite, similar to oil coke. The aromatic specifics of phytofulgurite are determined by its origin, when the basic substance was represented by humus organic matter with a substantially aromatic hydrocarbon framework. Our studies revealed the presence of diverse amino acids in the examined phytofulgurite material. It appeared that their total content (2.36 mg/g) is maximal for all the natural bitumens. It should be noted that practically all amino acids are largely represented by L-modification (95%). Moreover, the latter is also dominant in other naphthoids (in naphthides, 85%). Thus, the powerful atmospheric electric discharge on the haycock provoked ultra-high-speed (almost lightning) transformation of high plant material, i.e., organic matter of humus origin, into pyrobitumen (naphthoid) corresponding to medium anthraxolite. It means that the multistage and long-term (in natural environments) process was realized almost instantly.

Texturally controlled U/Pb dating of rutile from the Ivrea Zone

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In general, granulite-facies rocks are good candidates for U/Pb rutile dating as they commonly contain rutiles with >10 ppm U. From an analytical point of view, such rutiles are a particularly attractive phase for laser ablation ICP-MS dating for two reasons: 1) they often form large, homogeneous single grains of >200 microns, therefore allowing large spot sizes and hence good precision and 2) they contain virtually no Th (Th/U ratios are commonly <0.001), hence allowing for common lead correction via ²⁰⁸Pb. The second point is especially relevant as ²⁰⁸Pb is c. 40 times more abundant than ²⁰⁴Pb and has no interferences with ²⁰⁴Hg in the argon gas. With the analytical strategies outlined above, U/Pb rutile analysis offers new aspects for dating granulites. Single grain analysis of regular thin sections allows controlled dating both texturally and chemically.

Rutiles from granulite-facies metapelites of the Ivrea Zone exhibit a range of different textures. Infiltrating fluids partly recrystallized large rutiles in the matrix, while rutiles included in garnet are less affected, although not completely shielded [1]. Texturally-controlled dating revealed significantly younger ages of the obviously earlier grown rutiles (inclusions) compared to later grown rutiles (in matrix). This observation suggests that the U/Pb ages of these rutiles are not crystallization ages. Instead, a correlation of U/Pb age with crystal size (inclusions are generally smaller than matrix rutiles) seems to hint towards a diffusion-controlled mechanism (see Schoene & Bowring [2]) for controlling the ages of Ivrea Zone rutiles. The large spread in ages (ranging from ca 165 to 190 Ma; +/-5 Ma 2s) either indicates slow cooling rates (ca 2°C/Ma) in the Ivrea Zone or faster cooling rates with a heat pulse at ca 190 Ma, perhaps associated with Tethyan rifting [3].

[1] Luvizotto & Zack (submitted) *Chem Geol* [2] Schoene & Bowring (2007) *Geochim. Cosmochim. Acta* **71**, 165-185.

[3] Handy, Franz, Heller, Janott & Zubriggen (1999) *Tectonics* **18**, 1154-1177.