

## Automated $\gamma$ -ray spectrometer for monitoring wastes made by non-nuclear industries

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The huge amount of naturally occurring radioactive material (NORM) worldwide generated shows a high level of complexity for disposal purposes because of the high variability of radioactivity enrichment, therefore a case-by-case control is required. We developed a fully automated high-resolution gamma-ray spectrometer, called MCA\_Rad system [1], which offers a suitable measurement technique for monitoring huge amounts of NORM. Two coupled HPGe detectors p-type with 60% relative efficiency are accurately shielded allowing to reach an environmental background reduction of two orders of magnitude. Through fully automation of operational processes up to 24 samples can be measured without any human attendance. The absolute efficiency of the MCA\_Rad system is estimated by using two point sources, <sup>152</sup>Eu and a <sup>56</sup>Co and validated at 5% of relative uncertainty by measuring certified reference materials.

[1] G. Xhixha *et al.*, 2013 J Radioanal Nucl Chem 295:445–457. doi: 10.1007/s10967-012-1791-1

## Study on sulfur isotopic composition of acid rain in Nanchang City, China

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The acid rain is sulfuric acid type acid rain in Jiangxi province Nanchang City, its sulfur isotopic composition are different from that of other Cities.

We analyzed the sulfur isotopic composition of rain water from Nanchang City in this paper (Fig 1). The results indicated that the sulfur isotopic composition possesses a seasonal variation trend, isotopically heavier in spring and summer, lighter in autumn and winter. The sources of sulfur in rain water include bio-organic sulfur, anthropogenic sulfur and sulfur from the sea. In spring and summer, the sulfur in rain water comes mainly from anthropogenic sulfur. In autumn and winter, the sulfur in rain water dominantly originates from bio-organic sulfur. The sulfur in rain water from the sea may be very small in percentage.

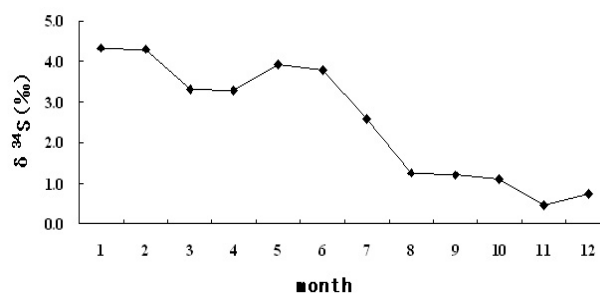


Fig. 1. Seasonal variations in sulfur isotopic composition of the precipitation

This research was jointly supported by the National natural Science Foundation of China (Grant No. 40963004).

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## A pathway for aromatic hydrocarbon formation

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Though aromatic hydrocarbons, the important components in petroleum, have been studied extensively, their formation mechanism is poorly understood, except for aromatic steranes, aromatic hopanes, and some sulphur-containing biomarker compounds, which are mainly thiophenes[1]. It is difficult to make clear their formation mechanism by studying the natural aromatic hydrocarbons lonely. During researching on the reaction of sulphur with organic matter by experiment, we found another pathway for aromatic hydrocarbon formation besides the aromatization of cyclanes. Though saturated chain compounds are difficult to become aromatic hydrocarbons, they can react quite easily with elemental sulphur and generate almost all kinds of aromatic hydrocarbons found in petroleum or sediments.

Many researchers have studied the mechanism of natural sulphur incorporation into organic matter by simulation or pyrolysis reactions[2], but the role of sulphur to the formation of common aromatic hydrocarbons in petroleum has not been pay great attention to and the action of sulphur on the organic matter in sediment used to be considered incorporating into carbon skeleton and forming sulphur-containing organic compounds even though Tissot *et* noted that the quantities of aromatic hydrocarbons in petroleum were direct proportion to sulphur[3]. From the present simulation experiment, it is clear that the reaction of sulphur and organic matter not only gives rise to sulphur-containing compounds, but also form non-heterocyclic aromatic hydrocarbons. Natural sediments are rich in saturated compounds and sulphur, so the reaction between them may be one of the most important sources of aromatic hydrocarbons.

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## The P-T-t path of the UHT granulites from Tongbai orogen, Central China

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Although the U-Pb zircon geochronometer has been widely used for dating metamorphism in moderate- to high-grade rocks, it is generally difficult to link the U-Pb age of zircon to pressure-temperature (P-T) conditions. Fortunately, the textures and chemical compositions (e.g. REEs) of zircon may provide qualitative information for correlating radiometric ages with certain stages in the metamorphic history of a rock. Additionally, zircon Lu-Hf isotopes can be used to constrain the nature of the igneous or metamorphic event in which the zircon grew.

Four stages of metamorphism are recognised in the granulites from Tongbai orogen, including a prograde stage (M1, ca.730–820°C at ca. <6 kbar), peak stage (M2, >920°C and 8.5–9.5 kbar), amphibolite facies retrograde stage (M3, ca. 700°C at ca. 7 kbar) and greenschist facies retrograde stage (M4, ca. 500 °C at ca. 5.8 kbar). Correspondingly, four distinct domains in the metamorphic zircons, which <sup>206</sup>Pb/<sup>238</sup>U age are ca. 443 Ma, ca. 430 Ma, ca. 419 Ma and ca. 400 Ma respectively, are classified based on CL images, trace elements, U-Pb ages and Hf isotopes. The ca. 443 Ma zircons, which are suggested as the M1 minerals, are characterized by flat HREE pattern, indicating presence of garnet during formation of these zircons. The ca. 430Ma zircons from a semi-pelitic granulite are characterized by strongly depleted HREEs, resulting in low HREE partitioning between zircon and garnet (<1.0), which is consistent with the characteristics of the ultra-high temperature metamorphic zircon. The age of ca. 430 Ma is represented the peak metamorphic age. The ca. 419 Ma zircons occur as rim of the ca. 430 Ma or ca. 443 Ma zircons from a semi-pelitic granulite, and are characterized by relatively rich in HREE. This coincides with the fact of that garnet porphyroblasts were replaced by biotite + plagioclase during the retrograde stage (M3). In a mafic rock, the ca. 400 Ma zircon rims have obviously lower initial <sup>176</sup>Hf/<sup>177</sup>Hf ratio than ca. 419 Ma zircons. It is extremely possible that hydrothermal fluids with low <sup>176</sup>Hf/<sup>177</sup>Hf ratios were added into the rock during greenschist-facies hydrothermal event at ca. 400 Ma. We argue that the Tongbai UHT granulites is possibly related to the mid oceanic ridge subduction.

## Stable Nitrogen Isotope Analysis of Amino Acids by GC/C/IRMS

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Measurements of the  $\delta^{15}\text{N}$  values of individual amino acids have provided very specific information about the biogeochemical, environmental, and ecological processes. The combination of gas chromatography with IRMS has become a hopeful tool for nitrogen isotopic analyses of individual amino acids in mixtures.

Amino acids before isotopic determination need to be derivatized using MTBSTFA and separated by gas chromatography, and gas chromatographic effluents were combusted and sent to the mass spectrometer continuously in a helium carrier stream. The GC column temperature was programmed for the tBDMSi derivatives separation as follows: isothermal 90 °C for 1 min, then heating up to 140 °C at rate of 8 °C/min and keeping it for 5 min, to 220 °C at rate of 3 °C/min and then to 285 °C at rate of 12 °C/min, and hold at final temperature 285 °C for 12.5 min until the elution of the last component. In this study, 0.8 ~ 4.5 nmol of each of the 20 amino acids (Ala, Gly, Val, Leu, Ile, Pro, Asn, Met, Ser, Thr, Phe, Asp, Glu, Lys, Gln, Arg, His, Tyr, Trp and GABA) was injected for isotopic determination.

All the 20 derivatized amino acids could be completely resolved in 60 min by GC program. We found a high isotopic correlation ( $R^2=0.9987$ ,  $p<0.0001$ ) between the determined values and the real values for most of the amino acids except three amino acids (Asn, Gln and Arg) which signals were much depleted. But for the three amino acids, there also existed a high isotopic correlation ( $R^2=0.9999$ ,  $p<0.0001$ ). Reproducible  $\delta^{15}\text{N}$  values were obtained within different injected amounts. The reproducibility of all the 20 derivatives was between 0.3‰ and 0.8‰. The mean precision of reproducibility was 0.5‰. After calibration with the 2 correlation equations, the isotopic difference between the calibrated values and the real values was in the range of 0.1‰ to 0.5‰ for the 20 amino acids.

Using the method developed, we successfully analysed the  $\delta^{15}\text{N}$  values of 20 free amino acids in tree leaves and barks.

This study work was kindly supported by the National Natural Science Foundation of China through grants 41173027.

## Cell Alive System (CAS): A new method of core sample freezing for shore-based biological analyses and sample storage

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We report a novel freezing technology for the long-term preservation of seafloor core samples. Seafloor core samples recovered by scientific ocean drilling provide unprecedented opportunities to study deep seafloor life and biogeochemical cycles. For the future analyses of cores using newly developed life science technologies, archiving precious core materials under the appropriate condition is fundamental significant. Given such scientific requirements, the Kochi Core Center (KCC), one of the official core repositories of the Integrated Ocean Drilling Program (IODP), has started storing some biological core samples in -80°C deep freezers and/or in liquid N<sub>2</sub> tanks, so called "DeepBIOS" (Deep Biosphere Samples).

To keep quality assurance and control (QA/QC) of the DeepBIOS, the initial freezing process is a key: however, using the conventional way (e.g., quick transfer to deep freezer), it has been confirmed that formation of ice crystals decompose biological signatures. During the JAMSTEC *Chikyu* Expedition 905, we tested a new technology called "Cell Alive System (CAS)", which utilizes magnetic field to vibrate water molecule in the sample, following snap and hence uniform freezing of core samples at the supercooling temperature. The core samples from various depths were sub-sampled, and immediately frozen in the CAS system along with the standard freezing method under the temperature of -20°C, -80°C, and -196°C. Analysis of cell abundance showed that conventional freezing methods decreased the number of microbial cells, whereas the CAS freezing resulted in almost no loss of the cells. We also tested the paleomagnetic characteristics after the CAS freezing, indicating no or very little change in remnant magnetism. No visible changes in volume of sediment was observed after the CAS freezing. Consequently, our results indicate that the CAS freezing technique is highly useful for QA/QC of scientific frozen core samples to preserve intact biological signatures, as well as other non-biological characteristics, for the long-term storage.

## The transformation and co-evolution of archaea with its environment assessed by energy quantum

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Archaea are believed as key players in the biogeochemical cycling of basic elements such as carbon, nitrogen, and sulfur in various environments, yet the physiology and functions of many of them remain largely unknown mainly due to difficulties in cultivation and lack of genetic manipulation systems. By the combined utilization of high pressure bioreactors, together with OMICS enabled metabolic potential analysis, synthetic biological technologies, and single cell capturing and sequencing methods, our group aims to reveal the physiology, evolution and functions of some important archaeal groups in the deep-sea environments. As examples, we will highlight our recent progress in the systematic investigation and genetic engineering of piezophilic/thermophilic Thermococcales strains pool from deep-sea hydrothermal vents; and some novel understandings on the physiology, evolution and metabolisms of methane oxidizing archaea-bacteria syntrophic consortia. We propose a "Coevolution and Energy Quantum" (CEQ) theory as a guidance for mathematic model construction to understand the interaction and co-evolution of life and environment.

## Skarn Cu-Fe-Au deposits in the East Hubei ore cluster, Middle–Lower Yangtze River metallogenic belt

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The East Hubei ore cluster is one of most important skarn Cu-Fe-Au clusters in the Middle–Lower Yangtze River metallogenic belt (MLYR) because it contains >50 skarn Cu-Fe-Au deposits and over 800 km<sup>2</sup> of igneous rocks, which provides the best sample for studies on the origins of Late Mesozoic igneous and ore-forming event in the MLYR. With respect to mineral systems and metal associations, there are dominantly skarn Cu-Fe, Fe-Cu, Fe and Au deposits, which are all genetically associated with Late Mesozoic granitoids in the East Hubei. Previous studies mainly focused on individual skarn deposits, and comparatively studies among different skarn Cu-Fe-Au deposits have not yet been investigated.

There are similar compositions and mineral assemblages of skarn minerals, such as prograde garnet and pyroxene, among skarn Cu-Fe, Fe-Cu, Fe and Au deposits, and garnets and pyroxenes are dominantly andradite and diopside, respectively. In contrast, obviously differences between sulphur isotope and mineralized-related intrusions in different skarn types have been recognized: (1) The 137–144 Ma skarn Cu-Fe, Fe-Cu and Au deposits are genetically associated with 136–143 Ma diorite and quartz diorite, and the  $\delta^{34}\text{S}$  of pyrites and chalcopyrites range from -8 to +12‰; while the 132–133 Ma skarn Fe deposits are genetically associated with 127–133 Ma diorite, quartz diorite and granite, and the  $\delta^{34}\text{S}$  of pyrite range from +12 to +20‰. (2) The intrusions related skarn Cu-Fe, Fe-Cu and Au deposits show relatively high Sr/Y (25.1–201), and  $(\text{La}/\text{Yb})_N$  (8.1–173), and low Yb contents (0.34–1.93 ppm); whereas intrusions-related skarn Fe deposits show relatively low Sr/Y (0.66–75.3), and  $(\text{La}/\text{Yb})_N$  (2.3–30.0), and high Yb contents (1.07–5.17 ppm). It is proposed that the tationation of Cu, Fe and Au in the East Hubei ore cluster are possible related to different magma sources of intrusion and various evaporitic rocks involved in the formation of these skarn deposits.

## Multistage refertilization of an Archean peridotite massif, N. Qaidam orogen (NE Tibet, China)

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A garnet (Gt) -facies peridotite massif [1] was involved in the early Paleozoic North Qaidam orogeny that generated ultrahigh-pressure (UHP) rocks during the collision between the Qaidam and Qilian blocks, NE Tibet (China) [2]. Original dunite and harzburgite now enclose fertile lherzolite zones, secondary clinopyroxene (Cpx)-rich lherzolite/wehrlite layers and rare clinopyroxenite dykes. Re-Os isotopic analyses of Fe-Ni-sulfides from the peridotite give Re-depleted model ages up to 3.0 Ga, indicating an Archean origin.

Hf-Nd-Sr-O mineral isotopic data support multiple refertilization episodes for this Archean massif. Lu-Hf isotopic ratios of Gt and Cpx in the dunites distant from the fertile rocks give an isochron age of ~1.5 Ga, similar to their Hf depleted-mantle model ages, suggesting early Mesoproterozoic melt addition from depleted asthenosphere. Parallel layers of Cpx-rich peridotites and pods of Gt+Cpx occur within harzburgite and dunite. Lu-Hf and Sm-Nd isotopic signatures indicate the formation of these secondary peridotite layers and pods was related to a refertilization by basaltic melts from the asthenosphere at ~1.1-0.7 Ga. All peridotitic minerals have moderately evolved initial Sr isotopes (0.70358-0.70873), relative to primitive mantle. Whole-rock and mineral elemental compositions of phlogopite-bearing garnet pyroxenite dykes suggest derivation from arc-related melts. Their mineral Nd-Sr-O isotopic compositions imply an evolved source, probably from subducted continental crust. However, Lu-Hf isotopic data reflect an early Paleozoic depleted-mantle origin. U-Pb ages of zircon and Lu-Hf isochrons and model ages of Gt+Cpx both show that the intrusion of the pyroxenitic melts, derived from asthenosphere contaminated by continental crust, occurred in the early Paleozoic, related to the coeval North Qaidam orogeny.

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## Gas and Water Distributed Patterns and Influential Factors in the Tight Sandstone Gas Reservoirs of Upper Triassic Xujiache Formation in Hechuan Area of Sichuan Basin, China

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The gas and water distribute complicatedly within the Upper Triassic Xujiache-2 tight sandstone in the Hechuan area of Sichuan basin. The origin and formation of water in the gas reservoir is complex. Generally, the wells released gas initially but produced water instead or shut down soon after, and that affected the gas production. Understanding distributed pattern of gas-water and its main influential factors is benefit to the development solutions-making of gas reservoir, enhanced reserves estimation and exploitation profits of such gas reservoir. This paper discusses the correlation of gas-bearing capability with pore-throat size, permeability and porosity, on the basis of reservoir rock research, combined with core mercury injection experiment, gas relative permeability experiment, nuclear magnetic resonance and gas-driving water percolation experiment. We also carried out typical gas reservoir dynamic analysis and synthetic geology research, using single well testing and pilot production data. The conclusions are followings, 1) the pore structures of the Xujiache-2 tight sandstone are dominated by fine or micro-throats, with strong heterogeneity; 2) the gas saturation relates with permeability and pore throat size in the Xujiache-2 gas reservoirs; 3) the Xujiache-2 gas and water have four distribution patterns, i.e. gas reservoir, upper gas with lower water, upper water with lower gas, and gas and water at the same zone; 4) the main controls on the Xujiache-2 gas-water occurrence are gentle-slope setting, pervasively near-source gas charging and heterogeneity of the pore throat.

## Geochronology of ore-bearing andesite in the Kuozhenkuola Au deposit, Northern Xinjiang, China

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The Sawur gold belt is in the northern Xinjiang, China, which belongs to the central south region of the Central Asian Orogenic Belt. The Kuozhenkuola gold deposit is the largest epithermal gold deposit in this belt, which is spatially associated with andesite.

Zircon La-ICPMS U-Pb age of ore-bearing andesite we picked the ore-bearing andesite in the deposit district by detailed sampling. Furthermore, we tested the zircon U-Pb age of andesite is  $339.4 \pm 4.8$  Ma (MSWD=0.73) by La-ICPMS in Hefei University of Technology. The Kuozhenkuola Au-bearing andesite was intruded in Early Carboniferous Epoch.

The zircon U-Pb age of the mineralized andesite ( $339.4 \pm 4.8$  Ma) is similar to the mineralization age ( $332 \pm 2.02$  Ma) in Kuozhenkuola Au deposit within error [1], which indicate that Kuozhenkuola Au mineralization was genetically related to the andesitic magma [2]. In Eastern Sawur area, there several Au deposits are found through current exploration, including Berkesidai, Heishantou and Tasite Au deposits [3][4]. This geochronological result affords credit evidence to genetic research of the Early Carboniferous Au mineralization in the regional area.

This research was sponsored by Chinese National Science and Technology Program (2011BAB06B01).

[1] Shen *et al.* (2006) *Sawur Research Report* : 111-117 (in Chinese). [2] Shen *et al.* (2007) *Ore Geology Reviews* **32**: 207-226. [3] Yang *et al.* (2005) *Mineral Deposit*, **24(3)**: 242-263 (in Chinese). [4] Fan *et al.* (2007) *Acta Petrological Sinica* **23(8)**: 1901-1908.

## Plutonium Immobilization and Re-mobilization by soil mineral-organic matter matrix compounds in the Far-field of the Savannah River Site (SRS), USA

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Pu is believed to be essentially immobile due to its low solubility and high particle reactivity to mineral phase or soil organic matter. For example, in sediments collected from a region of SRS, close to a wetland and a groundwater plume, <sup>239,240</sup>Pu concentrations correlated with organic carbon contents. However, previous studies reported Pu can be transported several kilometers in surface water systems through wind/water interactions [2,3]. The role of natural organic matter (NOM) in immobilizing or re-mobilizing Pu thus has been demonstrated. It was found that partitioning coefficients ( $K_d$ s) of intact humic acids (HAs) were significantly higher than those were treated with HF, lowering chelating sites for Pu or hydrophobicity differences between the two types HAs.  $K_d$ s of Pu (IV) with HAs were higher at low pH (4.4) than those at high pH (7.1), in contrast to the observation of Pu sorption to most mineral phases [4], possibly caused by the increased solubility of HA under more alkaline conditions. Though the colloidal fraction of HAs only accounts for a minor fraction of total OC (<5%) at pH 4.4, Pu binding to HAs accounts for 61-83% of the total added Pu, indicating colloidal organic matter as the mobile Pu carrier in the wetland area. Lastly, <sup>239,240</sup>Pu concentrations were found to be positively correlated with particulate hydroxamate and nitrogen contents, indicating binding to siderophores.

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## Petrographical features of the Shilu Fe-polymetallic ore deposit in Hainan Province, South China: implication for ore-deposit type

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The Shilu Fe-polymetallic hematite-rich deposit is situated in the western Hainan Province of South China. This deposit is characterized by upper Fe-rich ores and lower Co-Cu-rich ores, which are mainly hosted within a dominantly metamorphosed submarine siliciclastic and carbonate sedimentary succession of the Proterozoic Shilu Group that has been metamorphosed to greenschist to amphibolite facies. Two types of metamorphosed BIFs, i.e. the quartz itabirites which contain alternating hematite-rich microbands with quartz-rich microbands, and the amphibolitic itabirites which comprise alternating millimeter- to a few tens meter-scale, Fe oxide (magnetite, hematite)-rich bands with calcisilicate (garnet + amphibole + pyroxene + epidote)-rich mesobands to microbands, have been identified within the Shilu Group. A Fe-Co-Cu-rich sulfide facies, represented by the stratabound Co-Cu ores, also characterizes alternating Co-bearing pyrite + Co-bearing pyrrhotite + chalcopyrite macro- to mesobands dominantly with dolomite + calcite ± amphibole and minor with sericite + chlorite + quartz macro- to mesobands. The relic oolitic, pelletoid, colloidal and psammitic textures, and bedding structures which most likely represent primary sedimentary structures often observed in the Shilu itabirites. Hereby, the precursor precipitates to the Shilu deposit are interpreted as Fe-Co-Cu-(Si)-rich chemical sediments intercalated or mixed with variable amounts of detrital components. Input of the Fe, Si, Co and Cu from a mixed source of weathered landmass and sea-floor-derived hydrothermal fluids into a continental margin marine basin separated from an open ocean in fluctuating redox state caused primary sedimentation of the Shilu itabirites and Co-Cu ores via hydrogenous-sedimentary processes. Further, we consider the Shilu deposit as a BIF (banded iron formation) ore deposit-type (Lake-Superior).

## Rapid recovery of seawater <sup>187</sup>Os/<sup>188</sup>Os after CAMP magmatism at Triassic-Jurassic boundary

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The Late Triassic–Early Jurassic (T-J) was a time of major global change. The end-Triassic mass extinction is one of the “big five” extinction events of the Phanerozoic. The extinction is proposed to be causally linked with volcanic eruptions from the Central Atlantic Magmatic Province (CAMP)<sup>[1][2]</sup> which produced low <sup>187</sup>Os/<sup>188</sup>Os ratios in seawater at the period boundary. Late Triassic to Early Jurassic organic-rich shales from SE Sicily offer an opportunity to track events across the T-J boundary. Here we present Re-Os geochemistry of Hettangian Streppenosa Formation black shales from Gela #1 drillcore, SE Sicily.

Black shales from the lower Streppenosa Formation, deposited in a deep euxinic intraplatform basin, yield a Model 3 Re-Os age of 200.3 Ma and initial <sup>187</sup>Os/<sup>188</sup>Os of 0.87. This Early Jurassic age is nominally younger than the T-J boundary of 201.3 Ma<sup>[3]</sup> and the major four pulses of CAMP volcanism, dated between 201.6 and 200.9 Ma<sup>[2]</sup>.

The seawater <sup>187</sup>Os/<sup>188</sup>Os ratio of 0.87 at 200.3 Ma is the highest ratio recorded in Triassic to Early Jurassic seawater<sup>[4]</sup>. This ratio stands in contrast to mostly low ratios reported across the T-J boundary, attributed to the sudden initiation of volcanic activity of CAMP<sup>[1][4]</sup>. Yet the high <sup>187</sup>Os/<sup>188</sup>Os coincides with an unusual spike in seawater <sup>187</sup>Os/<sup>188</sup>Os at the T-J boundary<sup>[4]</sup>. The high <sup>187</sup>Os/<sup>188</sup>Os ratio at 200.3 Ma documents minimal contribution of unradiogenic Os from CAMP magmatism, and may also reflect enhanced continental weathering resulting from uplift along newly formed rifted margins. This rapid recovery of seawater <sup>187</sup>Os/<sup>188</sup>Os after CAMP volcanic eruption likely reflects the short residence time of Os in seawater (tens of kyr).

Our results confirm that the Os isotope composition of seawater responds rapidly to large volcanic events, further demonstrating the role that seawater Os can play in identifying major environmental changes.

ENI S.p.A. provided samples and financial support.

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## Selenium geochemical characteristics of Ruorgai plateau wetland, eastern margin of the Qinghai-Tibet Plateau, Southwest China

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Ruorgai wetland is a typical plateau wetland ecosystem in the eastern margin of the Qinghai-Tibet Plateau, southwest China. This area is one of five big pastoral areas in China. On the other hand, the people's health and the development of livestock suffer from selenium deficiency symptom[1].

Here we developed a method for determination of selenium in environment sample by high performance liquid phase inductively coupled plasma-mass spectrometry (HPLC-ICP-MS)[2]. The selenium of rock, soil, water and plant in this area were researched. Conclusions are as follows.

The selenium of rock in this area is generally lower than the crustal abundance. The selenium of the water is much lower than normal drinking water. The selenium of plant is between selenium deficiency areas and normal areas. The selenium of increased with organic matter content in soil.

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## Fluid and melt inclusions in the Wulaga gold deposit, Heilongjiang, China

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The Wulaga gold deposit, located in northeastern China, is a controversial deposit for its ore genesis[1-3]. The ore bodies are mainly hosted in cryptoexplosive breccia zone within Tuanjiegou plagioclase granite-porphyry of 106~108Ma[4], and in the layer fractures of metamorphic Heilongjiang group. Gold mineralization can be divided into 3 stages: pyrite- early white chalcedony quartz stage (stage I), smoky gray chalcedony quartz - polymetallic sulfide stage (stage II), and carbonate-quartz stage (stage III). Fluid inclusions in stage I are mainly aqueous solutions with homogenization temperatures (Th) of 154°C~355°C, mainly in 230°C~270°C. Salinities of fluid inclusions are 1.3%~8.2%NaCl eqv. Those in stage II are 159°C~196°C, with salinities of 2.2%~3.2%NaCl eqv. Those in stage III are mainly in 170°C~230°C, with salinities of 0.5%~2.9%NaCl eqv. Ore-forming fluids in the main mineralization stages are characterized by mid to low temperatures, low salinities, and lack of CO<sub>2</sub>, which is similar with epithermal deposits related with continental volcanic-subvolcanic rocks. There are three types of inclusions in quartz phenocryst of plagioclase granite-porphyry, that is, melt inclusions, primary L-V and L-V-S inclusions, as well as secondary L-V inclusions. Glassy melt inclusions are characterized by acid magma (SiO<sub>2</sub> =69.5~73.8%), with the trapping temperatures higher than 800°C. Secondary L-V inclusions in quartz phenocryst have 210°C~350°C of Th, which are coincided with those of mineralizing stage I (Q1), while salinities (5~7wt%NaCleqv.) are slightly higher than those of Q1. Melt and fluid inclusion study shows that gold mineralization is related with plagioclase granite-porphyry, and it is possible for silicate magma to produce salt-aqueous solution through immiscibility in magmatic differentiation.

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## Relationships between porphyry Cu–Mo mineralization in the Jinshajiang–Red River metallogenic belt and tectonic activity: Constraints from zircon U–Pb and molybdenite Re–Os geochronology

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The Jinshajiang–Red River porphyry Cu–Mo metallogenic belt is an important Cenozoic porphyry Cu–Mo mineralization concentrating zone in the eastern Indo–Asian collision zone. New zircon U–Pb and molybdenite Re–Os ages and compilation of previously published ages indicate that porphyry Cu–Mo deposits in the belt did not form at the same time, i.e., the porphyry emplacement and relevant Cu–Mo mineralization ages of the Ailaoshan–Red River ore belt in south range from 36.3 Ma to 34.6 Ma, and from 36.0 Ma to 33.9 Ma, respectively, which are obviously younger than the porphyry emplacement ages of 43.8–36.9 Ma and the relevant Cu–Mo mineralization ages of 41.6–35.8 Ma of the Yulong ore belt in north. Tectonic studies indicated that the Jinshajiang fault system in north and Ailaoshan–Red River fault system in south of the Red river belt had different strike-slip patterns and ages. The right-lateral strike-slip motion of the Jinshajiang fault system initiated at ca. 43 Ma with corresponding formation of the Yulong porphyry Cu–Mo system, whereas the left-lateral strike-slip motion of the Ailaoshan–Red River fault system initiated at ca. 36 Ma with corresponding formation of the Ailaoshan–Red River porphyry Cu–Mo system. Therefore, the different ages of porphyry Cu–Mo systems, between in north and south of the Jinshajiang–Red River belt, indicate that the porphyry Cu–Mo mineralization is closely related to the divergent strike faulting resulted from the Indo Asian collision. The tanslithospheric Jinshajiang–Red River faulting caused partial melting of the enriched mantle sources of alkali-rich porphyries by depressurization or/and asthenospheric heating, and facilitated the migration of alkali-rich magmas and the corresponding formation of alkali-rich porphyries and relevant Cu–Mo deposits in the belt.

## The Platinum-Group Element Abundance Patterns of the Meishan Permian-Triassic Boundary, China

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It is a long-standing controversy what triggered the extinctions at the Permian-Triassic boundary, the most severe mass extinction in the geologic record (1). We analyzed all PGEs (except for Os) of a set of samples from the GSSP of the P-Tr boundary at Meishan, China. The PGE patterns have important constraints on sources of the P-Tr boundary materials. The data are also compared with previous results of known layers samples (2).

A total of 16 samples from three sections at Meishan were analyzed, which were numbered bed A to H, T, N, and bed O to S, and U. They were treated as blind testing samples, and the location information was released after the experiments. Our data reveal no significant positive PGE anomaly with the Ir contents of 0.003-0.029 ng/g. Compared with previous analyses (2), the abundance of PGEs reached the maximum at layer B-26. The layer B-25 and the pyrite lamina of B-24 (bed C and Q) that is referred to as the P-Tr event boundary, contain the lowest abundance of PGEs.

The P-Tr boundary samples show highly fractionated PGE patterns, distinct from chondrites and iron meteorites. The PGE patterns are parallel to those of Siberian flood basalts and Emeishan flood basalts, especially more similar to the former. The PGE data suggest a possible linkage between the P-Tr boundary event and the eruption of Siberian or Emeishan flood basalts.

[1] Erwin (1994) *Nature* 367, 231-236. [2] Xu *et al.*, (2007) *Chem. Geo.* 246, 55-64.

## Synthesis of Symplectite (Fe<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O)

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Symplectite is the crystalline-triclinic ferrous arsenate (Fe<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O). It has very low solubility at neutral to slightly alkaline pH (much lower than scorodite). Hence, symplectite could be a dominant compound for arsenic immobilization in suboxic environment, such as in co-precipitated tailings ponds. However, little is known about its synthesis, solubility and structure. The objectives of this work were to study the synthesis methods and to characterize the product using various techniques.

Fe(II) (FeSO<sub>4</sub>·7H<sub>2</sub>O, 60, 90 mM pH 2, adjusted by HNO<sub>3</sub>) and As(V) (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O, 40, 70mM, pH 8.6) solutions ere prepared using deoxygenated DI-water in glovebox.

Different synthesis strategies were tested including raising the pH of pre-mixed Fe(II)-As(V) solutions to 4, 5, 6, 8 respectively (denoted as RMP), and mixing Fe(II) and As(V) solutions at fixed pH (4, 5, 6, 8) (denoted as TAP) to precipitate the precursor followed by aging at different temperatures (21, 45, 70 °C). The molar ratio of Fe/As = 1.5 was applied. NaOH (0.25N) and HNO<sub>3</sub> (0.5N) were used to adjust media pH. The solid products were separated by filtration in glovebox and vacuum dried. XRD and SEM were used to characterize the products.

The XRD data indicated the successful synthesis of symplectite. SEM showed that the product was needle-shaped particles. The TAP method is better than RMP for the synthesis of symplectite. The media pH and temperature for precursor precipitation or crystallization during ageing are very important factors. Better crystallinity was obtained at higher temperature. The pH significantly influences the product's purity and re-crystallization. The rate of re-crystallization increased with increasing pH, but the highest pH of 8 was applied to avoid the formation of Fe(OH)<sub>2</sub>.

[1] R.B. Johoston. Solubility of symplectite (ferrous arsenate):Implication for reduced groundwaters and other geochemical environments. Soil Sci. Soc. Am. 2007, 71:101-107.

## In-situ trace elements and Li, Sr isotopes in peridotite xenoliths from Kuandian, North China Craton: Insights into Pacific slab subduction- related mantle modification

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Trace element, Li and Sr isotopic compositions of major minerals in peridotite xenoliths from Kuandian, North China Craton (NCC) were analyzed *in situ* to investigate Pacific slab subduction-related mantle modification beneath the eastern NCC. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios are positively correlated with the La/Nb, Ce/Zr and Sr/Y ratios and negatively correlated with the Nb/U ratio for Cpx. Based on the trace element distribution patterns, three types of Cpx were identified. Type 1 Cpx are characterized by significant Nb-Ta-Ti depletions and the highest Sr isotopic ratios; Type 2 Cpx display Nb (or Ta) depletions and highly variable Nb and Ta fractionation; and Type 3 Cpx show no significant Nb or Ta depletion or even weak Ta enrichment and have the lowest Sr isotopic ratios. Some Cpx display a pattern of increasing Ca+Mg±Si from the cores to the rims, indicating addition of Ca+Mg±Si-rich fluids derived from a serpentinized peridotite layer above the subducting slab. These features indicate multiple mantle metasomatism events associated with the ancient subduction of the altered Pacific oceanic crust, which may contribute substantially to the destruction of the eastern NCC.

The Li contents in the Cpx (up to 34.8 ppm) and Opx (up to 28.0 ppm) are typically higher than those in the coexisting Ol (< 9.19 ppm), suggesting silicate melt metasomatism. Furthermore, both pyroxenes and Ol display remarkable zoning patterns in their Li contents and isotopic ratios, indicating a redistribution and disequilibrium fractionation of Li within and/or between minerals. The Li enrichment and low δ<sup>7</sup>Li values in the rims of most Ol, Cpx and Opx may have arisen from diffusive fractionation during Li-rich melt/fluid metasomatic processes. However, the Li depletion and high δ<sup>7</sup>Li in the rims of a few Ol may suggest cooling-induced Li isotope fractionation. Based on the zonation and Li diffusion coefficient at mantle temperatures, a model calculation suggests that the latest Li-rich melt/fluid metasomatic process was a recent event occurring shortly before or during the host magma eruption.

## Temporal variations of Fukushima-derived $^{129}\text{I}$ in precipitations

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The precipitation samples collected from Fukushima, Japan over 2010-2012 were analyzed for  $^{127}\text{I}$  and  $^{129}\text{I}$  in order to explore the atmospheric level and behaviour of radioactive iodine released from the Fukushima nuclear accident in 2011.  $^{129}\text{I}$  concentration of  $1.2 \times 10^8$  atom/L in 2010 before the accident dramatically increased about 4 orders of magnitude to  $7.6 \times 10^{11}$  atom/L in March 2011 immediately after the accident with a  $^{129}\text{I}/^{127}\text{I}$  ratio up to  $6.9 \times 10^{-5}$ . Afterwards the  $^{129}\text{I}$  concentrations in precipitation decreased exponentially to  $\sim 3 \times 10^9$  atom/L until October 2011 with a half-life of about 29 days. This decline trend of  $^{129}\text{I}$  concentrations in precipitation was interrupted around October 2011 by newly  $^{129}\text{I}$  input to the atmosphere, and the elevated  $^{129}\text{I}$  concentration in the atmosphere decreased exponentially again. Such a cycle of abrupt increase - exponential decrease occurred three times until present. This temporal variation can be attributed as alternation of  $^{129}\text{I}$  dispersion and re-suspension from the contaminated local environment. A  $^{129}\text{I}/^{131}\text{I}$  atomic ratio of  $16 \pm 1$  obtained from the rainwater sample is comparable with those estimated by analysis of surface soil samples [1]. Comparison of  $^{129}\text{I}$  level in Europe suggests an insignificant effect of  $^{129}\text{I}$  released from Fukushima to the  $^{129}\text{I}$  level in the Europe.

[1] Miyake *et al.* (2012) *Geochem. J.* **46**, 327-333.

## Historical trends of heavy metal pollution recorded in sediments from Lake Qionghai, China

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Heavy metals are serious pollutants due to their toxicity and long persistence in the environment. Lake sediment cores preserved the geochemical environmental changing record. A sediment core was collected in 2011 from Lake Qionghai, the second largest freshwater lake of Sichuan Province in China, to analyze the heavy metal pollution evolution of the lake.

The sediment core was 46cm in height, and was sectioned at 1cm intervals for the above 30cm while 2cm intervals for the left. The coefficients of variation of As, Cd, Cr, Cu, Hg, Ni, Pb, Zn in the sediment core are 0.32, 0.72, 0.16, 0.08, 0.34, 0.24, 0.19, 0.19, respectively, which indicates Cd varies greatly as a result of human activities, while the other heavy metals have little change mainly due to a natural origin.

The content of Cd increased distinctly and continuously to 0.87g/kg in the surficial six centimetres of the sediment core, indicating the lake had a large quantity of Cd input in the last years. According to the  $^{137}\text{Cs}$  dating result, this interval was deposited from 1998 to 2011. Besides, the evaluation by potential ecological risk index method showed Cd in the sediments had pollution risk of medium degree. That means the lake has suffered Cd pollution since 1998.

## **Spatial-temporal extent of the influence of the Mongol-Okhotsk tectonic regime on China during Mesozoic: Evidence from Mesozoic igneous rocks**

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It has been a controversial issue whether the southward subduction of the Mongol-Okhotsk oceanic plate happen during Mesozoic. The spatial-temporal distributions of the Mesozoic igneous rocks in NE China provide a constraints on this question. Zircon U-Pb dating results indicate that the Mesozoic magmatism in the Argun Massif adjacent to the Mongol-Okhotsk suture can be subdivided into the following stages: ~245 Ma, ~220 Ma, ~200 Ma, ~185 Ma, ~162 Ma, ~142 Ma, and ~125 Ma. The Early Mesozoic igneous rocks (~245 Ma, ~220 Ma, ~200 Ma, and ~185 Ma) consist of a suite of calc-alkaline basalt, basalt-andesite, diorite, and granodiorite. Together with the coeval porphyry Cu-Mo deposits, they reveal the subduction of the Mongol-Okhotsk plate beneath the Argun Massif. The ~162 Ma igneous rocks are composed of trachy-basalt, basaltic trachyandesite, and trachyandesite which display a transitional type between alkaline and subalkaline series, and only occur in the Great Xing'an Range and northern Hebei-western Liaoning provinces. Similarly, ~142 Ma magmatism also only occur in the same area as ~162 Ma igneous rocks and consist of alkaline rhyolite, implying an extensional environment. Taken together, it is suggested that the ~162 Ma and ~142 Ma magmatism could be related the evolution of the Mongol-Okhotsk tectonic regime and could be generated by the collapse and/or delamination of the thickened lower crust in the Great Xing'an Range and northern Hebei-western Liaoning provinces, which is also supported by two regional unconformability (beneath the Haifanggou Formation and overlying the Tuchengzi Formation, respectively). From north to south, the beginning time of ~162 Ma and ~142 Ma magmatism gradually become younger, further implying that their formations should be attributed to the evolution of the Mongol-Okhotsk tectonic regime. The ~125 Ma igneous rocks are widely distributed in NE China and consist of bimodal igneous rocks in the Great Xing'an Range and Songliao basin as well as a calc-alkaline volcanic rocks in the eastern Heilongjiang-Jinlin provinces, suggesting that the later could be formed under the subduction of the Paleo-pacific plate beneath the Eurasian continent, whereas the former could be generated by the delamination of the thickened lower crust and/or the subduction of the Paleo-pacific plate. This work is supported by 973 program (2013CB429803) and NSFC (41272077).

## **Tectonic implications for Mid-late-Neoproterozoic rift-related volcanic rocks in China**

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Mid-late-Neoproterozoic rift-related volcanic rocks which had aggregated to form part of the Rodinia Supercontinent by ca. 900 Ma are widespread on several Precambrian in China. These volcanic rocks, which mainly consist of huge volumes of basic rocks and variable amounts of silicic volcanics, with small amounts or absence of intermediate rocks displaying a compositional bimodality, have attracted a number of recent studies. Several lines of evidence show most of these volcanics have a compositional bimodality, and formed in an intra-continental rift setting which may be genetically linked with mantle plumes activities.

On the basis of petrogeochemical data, these basic lavas can be classified into two major types: High Ti/Y and Low Ti/Y types, both of which can be further divided into two subtypes by different Nb/La ratios, respectively. The lavas (Nb/La <0.85) can be accounted for by lithospheric contamination of asthenosphere- (or plume-) derived magmas during their ascent, but parental magmas of others (Nb/La >0.85) may have not undergone such a process.

The rift-related volcanism at end of mid-Neoproterozoic and early-Cambrian coincided temporally with the separating between Australia-East Antarctica, South China and Laurentia and between Australia and Tarim, respectively. The mid-late-Neoproterozoic volcanism in China is the geologic record of broken-up of the supercontinent Rodinia. (This research is supported by Land and Resources Survey Project of China, Grant No. 1212011220649 and the National Natural Science Foundation of China, Grant No. 40872061)

## Vanadium dynamics in soils impacted by vanadiferous titanomagnetite ore mining

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Vanadium (V) plays a highly critical role in natural systems due to its potential essence and toxicity to organisms. To date, knowledge about V biogeochemistry is scarce so that assessing the impact of V enriched solids on the terrestrial environment is still difficult. Two soil profiles overlaid with and without ores and mining rests close to the vanadiferous titanomagnetite ore mining site were sampled. We attempted to characterize the mobility of soil V under the influence of mining activities and to estimate the potential risk of V to the adjacent environment by analysing the vertical V distribution, speciation of V oxidation state and its sequential distribution in different organic and mineral fractions. Additionally, HPLC-ICP-MS coupling was taken for speciation of V(V) and V(IV) in water and EDTA extracts of soils to understand V bioavailability and its potential toxicity.

Except the very high V concentrations (784 ppm) in the surface layer composed of mining rests, the soil V concentrations vary little along both soil profiles (343-356 and 143-201 ppm), suggesting the general low V mobility. Speciation of soil V based on sodium carbonate extraction indicates that more than 85% of total V in soil is tetravalent, which is generally rather insoluble and strongly absorbed [1]. Results of sequential extraction show totally different fractionation patterns compared to the other metalloids e.g. arsenic. Vanadium prefers to enrich in crystalline fractions and residues, while arsenic is abundant in poorly crystalline fractions. Interestingly, the proportion of V in the crystalline fraction and residues is independent of the depth (~69%) in the unpolluted soils, but the relevance of these two fractions increases from 52% to 82% with the depth along the polluted soil profile, suggesting the potential influence of mining materials on V binding forms in soils. Pentavalent V predominates in both water and EDTA extracts, reflecting higher mobility of V(V) than V(IV). This further implicates elevated toxicity for the plants and soil organism due to higher toxicity of V(V) compared to V(IV).

[1] Wehrli & Stumm (1989) *GCA* 53, 69-77.

## Paleoclimate reconstruct of Late Triassic Xujiahe Formation Sichuan Basin in Southwest China

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Formation of Upper Triassic in Sichuan Basin China is abundant in gas resource, with proved gas resource of more than hundreds of billion cubic meters. As a result, the formation has become an important area for the gas industry of China.

Xujiahe Formation can be divided into six members with a texture of interbedded sandstones and mudstones, like a sandwich. The paleoclimate is an important reason for the texture. Three methods named palynoflora, clay minerals, and eigen elements were used in this paper to reconstruct the paleoclimate when Xujiahe Formation was sediment. Mudstone samples of the six members were taken from six different areas of the entire basin, and then analyzed to reconstruct the paleoclimate, respectively. The palynoflora indicated that the paleoclimate background of Xujiahe Formation was hot and humid, belonging to tropics-subtropics zone. Making use of clay minerals, the ratio of Kaolinite and Illite (K/I) was used to analyze the Paleoclimate, which reduced the ambiguity. Using the ratio of Calcium and Magnesium (Ca/Mg) and Strontium/Barium (Sr/Ba), the details of paleotemperature and paleomoisture (paleosalinity) were analyzed. It can be seen that the paleotemperature and paleomoisture of Xujiahe Formation fluctuated regularly against the setting of tropics-subtropics. Member Xu 1 was formed in transitional facies when the paleoclimate was hot and humid. Member Xu 2 was formed in the climate of hot and arid. When member Xu 3 was formed, the temperature and moisture were all higher than Xu 2. It belonged to palustrine environment. After shortly decrease of temperature and moisture in Member Xu 4, it became hottest and wettest during the period when Member Xu 5 was formed. The temperature and moisture declined slowly in Member Xu 6, and the paleoclimate became relatively warm and aridity. It is the fluctuation of paleoclimate that led to the forming of the sandwich sedimentation structure of Xujiahe Formation in Sichuan Basin Southwest China.

## The nature of crustal components in mantle sources for Cenozoic continent basalts in southeastern North China Craton

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Cenozoic continental basalts in the southeastern part of the North China Craton exhibit depleted Sr-Nd isotope compositions and OIB-like trace element patterns. It is intriguing what kinds of crustal component were involved in mantle sources for the intraplate basalts. An integrated interpretation of major-trace elements and stable-radiogenic isotope data for these intraplate provides new insights into this issue. Different types of correlations occur between such variables as Ba/Th, Sr/Y,  $\epsilon_{Nd}(t)$ , (La/Yb)<sub>N</sub> and SiO<sub>2</sub>, suggesting two types of crustal components in the mantle source: altered oceanic basalt and seafloor sediment. The altered oceanic basalt yields adakitic melt that is characterized by high (La/Yb)<sub>N</sub>, Sr/Y and  $\epsilon_{Nd}(t)$  but low Ba/Th and SiO<sub>2</sub>, whereas the seafloor sediment yields sialic melt that is characterized by low (La/Yb)<sub>N</sub>, Sr/Y and  $\epsilon_{Nd}(t)$  but high Ba/Th and SiO<sub>2</sub>. The OIB-type trace element patterns are interpreted as involvement of the oceanic crust that underwent partial melting outside the rutile stability field. These basalts exhibit low Fe/Zn and high Fe/Mn ratios, suggesting pyroxene-rich source lithology. The depleted Sr-Nd-Hf isotope compositions indicate involvement of juvenile lithospheric mantle.

We propose that westward subduction of the Pacific plate beneath the Eurasian continent serves as the geodynamic mechanism for slab-mantle interaction in oceanic subduction channel for formation of the mantle sources. A MASH mechanism is used to account for petrogenesis of these continental basalts. The subduction-modified oceanic basalt and sediment become melted (M) during subduction to mantle depths of over 100 km. Then the melts assimilated (A) the SCLM wedge peridotite to generate a variety of ultramafic metasomes. These metasomes would be stored (S) at bottom of the SCLM wedge for a long time (maybe 50-100 Myr or longer). Finally, when the continental lithosphere was in extension during the renewed subduction of Pacific plate beneath the Eurasian continent in the Cenozoic, these metasomes were heated (H) by upwelling of the asthenospheric mantle, generating the intraplate basaltic melts.

## Evidence for the hydrothermal fluid origin of Sanqisan uranium deposit in China

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Sanqisan uranium deposit is a typical carbonate-siliceous-pelitic rock-type uranium deposit in Southwestern Guangxi. Through studies of the ore geological features, trace elements, isotope geochemical characteristics and petrology, this paper presents the evidence of hydrothermal activities, and draws the conclusions that magmatism has great significance for the formation of Sanqisan deposit, with the general basic geological features the same as the normal hydrothermal type uranium deposits. 1) Many siliceous bodies, as well as the multiphase quartz vein, have been found in field. The siliceous bodies, with a relatively high uranium content, appear in lenticular shape and a different scope, the big one being 2-3 m thick, 5-6 m long, the small one being only dozens of centimeters. 2) According to microscopic observation, the newly found pyroclastic and phyllite detritus indicate that there are signs of magma activity (or volcanic activity), and show that the main ore-bearing structure is relatively violent with large scale. 3) There are signs of multiphase hydrothermal activity, such as quartzitification, pyritization, carbonatization, etc., which intersperse with each other. 4) From the trace element analysis results, the content of some elements, such as Ni, As, Mo, Zn, Cd, Co, etc. are significantly high, more than 10 to hundreds times higher than the crustal abundance value, and the concentrating coefficient of Sb is 4630. 5) The carbon and oxygen isotopic compositions of hydrothermal calcite of the Sanqisan deposit show obvious genetic characteristics of deep magmatic source. The variation range of  $\delta^{13}C$  is -0.709‰~ -3.172‰, and that of  $\delta^{18}O$  is -12.451‰~ -14.516‰. 6) According to the U-Pb zircon dating, the ages for the diabase dykes in Sanqisan uranium deposit are 90Ma and 32-47Ma, which are in accordance with the age of the Sanqisan uranium deposit, indicating great significance of magmatism for the mineralization of Sanqisan deposit.

This work is supported financially by the National Natural Scientific Foundation of China (Grants No. 41173059).

## Ca<sup>2+</sup> and Phosphate Ion Transport To and Calcium Phosphate Cluster Nucleation Within Collagen Fibrils In Bone Biomineralization

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Bone is a composite material consisting of collagen, an insoluble, fibrillar, protein; a non-stoichiometric calcium phosphate (Ca-P) phase idealized to hydroxyapatite (HAP); and soluble proteins. Based on TEM observations for six decades, collagen fibrils are known to be arranged in a hierarchical, “staggered” array, which controls the locations of the earliest nucleation in “hole zones” of the “a and e bands” within the fibril. However, the mechanisms for Ca<sup>2+</sup> and inorganic phosphate (P<sub>i</sub>) ion transport into the fibrils and for Ca-P nucleation in specific locations remain unknown.

We used the structure of collagen mimetic peptides and the 3-D packing structure of collagen molecules within a fibril to construct and optimize the entire collagen fibril structure with regular Molecular Dynamics (MD) simulations. Furthermore, Ca-P cluster formation and water diffusion and density distributions within the fibril were determined using Hamiltonian Replica Exchange Molecular Dynamics (HREMD), which captures even rare nucleation events. Significantly, we found that the lateral space between two adjacent collagen molecules is too small to allow prenucleation clusters larger than ~1nm to enter the fibril and reach the hole zones near the a and e bands where the earliest nucleation is observed by TEM. This result provides constraints on previously proposed mechanisms for calcium phosphate prenucleation cluster transport into the intra-fibrillar space. Further, the charged amino acid side chains (glutamate, aspartate, lysine, arginine) of the e bands are oriented to point into the hole zones, and attract Ca<sup>2+</sup> and P<sub>i</sub> ions electrostatically to form the earliest Ca-P clusters. We have shown for the first time the mechanisms by which the 3D hierarchical structure of collagen controls mineral nucleation from the Å – 10s of nm length-scale.

## Carbonate speciation in depolymerized silicate melts (glasses): New evidence from ab initio calculations and <sup>13</sup>C MAS and static NMR measurements

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Knowledge of the dissolution mechanisms of CO<sub>2</sub> in silicate melts and glasses is indispensable for understanding its effects on physical and thermodynamic properties. For depolymerised silicate compositions, previous IR, Raman and <sup>13</sup>C MAS NMR studies of quenched glasses all revealed CO<sub>3</sub><sup>2-</sup> as the dominant species. However, no consensus has been reached as to whether CO<sub>3</sub><sup>2-</sup> are linked to network-formers (e.g. Si) or bonded to network-modifiers (e.g. Ca) only (referred to as free carbonates hereafter), due to the lack of direct information for spectroscopic features of the former.

Here we report ab initio calculation results (using Gaussian 09) of vibrational frequencies (at B3LYP/6-31+G(d,p), scaled by 0.9685) and <sup>13</sup>C chemical shift tensors (at HF/6-311+G(2df,p)) for CO<sub>3</sub><sup>2-</sup> groups bonded to one and two SiO<sub>4</sub>/AlO<sub>4</sub> tetrahedra. We also report <sup>13</sup>C MAS and static NMR results for several <sup>13</sup>CO<sub>2</sub>-bearing depolymerized silicate glasses, e.g. diopside (CaMgSi<sub>2</sub>O<sub>6</sub>) and Ca-melilite (Ca<sub>1.5</sub>AlSi<sub>2</sub>O<sub>7</sub>), prepared by quenching melts at 1.0-1.5 GPa and 1400-1600 °C in a piston cylinder apparatus. The ab initio calculation revealed that the splittings of the ν<sub>3</sub> (asymmetric stretching) doublets for CO<sub>3</sub><sup>2-</sup> bonded to one or two tetrahedral Si/Al are all large (around 180-480 cm<sup>-1</sup>). In contrast, experimental data for CO<sub>3</sub><sup>2-</sup> (bonded only to metal cations) in minerals show ν<sub>3</sub> splitting from zero to moderate, depending on local geometry. Thus, the moderate ν<sub>3</sub> splitting (70-100 cm<sup>-1</sup>) reported for many depolymerized silicate glasses, which was used as evidence for CO<sub>3</sub><sup>2-</sup> bonded to one Si (e.g. [1]), should be better viewed as evidence for free carbonates. Our calculations also showed that carbonates bonded to one or two Si/Al all show distinctly different characteristics of <sup>13</sup>C chemical shift tensors compared to free carbonates, similar to experimental observations for organic carbonates (bonded to one or two C). Our <sup>13</sup>C MAS and static NMR data for depolymerized silicate glasses are consistent with free carbonates as the dominant species. Its formation would lead to polymerization of the silicate structure.

[1] Blank, JG & Brooker, RA (1994) *Rev. Mineral.* **30**, 157-186.