

## Geochemistry of loess sections from high altitude region, Yili Basin, NW China

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Yili Basin is located in the northwest of China, where loess deposits up to several ten meters are exposed. As controlled by the westerly circulation in and year out, the modern climate is different from the other loess distribute areas in China. In this study, we selected two loess-paleosol sections from step zone, Kuerdenengbulake Section (43°29'N, 83°58'E), and desert step zone, Zeketai Section (43°32'N, 83°19'E), for systematic geochemical studies, such as major elements, trace elements and REE abundances, Rb-Sr, Sr-Nd and Sm-Nd isotope systems.

Based on the major and trace element abundance, the paleosols from steppe zone can be distinguished from the loess by decarbonation and higher contents of stable and relatively stable elements, such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, K<sub>2</sub>O and Rb, whereas the paleosols from desert steppe zone do not show distinct difference of major and trace elements concentration between loess and paleosols. Pedogenesis is thought to be influenced strongly by climate, especially by precipitation.

REE patterns of Yili loess and paleosols are remarkably uniform with (La/Yb)<sub>N</sub> ≈ 7.6, this value is smaller than that of the upper continental crust (UCC), (La/Yb)<sub>N</sub> ≈ 9.0. Negative Eu anomalies, expressed in Eu/Eu\* ratios vary from 0.61 to 0.82.

Rb-Sr isotopic systematics of the loess-paleosols show a well-correlated pseudo-isochron, which reflects the mixing of two components, i.e., the silicate material with high <sup>87</sup>Rb/<sup>86</sup>Sr ratios and high <sup>87</sup>Sr/<sup>86</sup>Sr ratios and the carbonate materials with low <sup>87</sup>Rb/<sup>86</sup>Sr and low <sup>87</sup>Sr/<sup>86</sup>Sr (0.710).

Neodymium isotopic compositions of Yili loess-paleosols are uniform with ε<sub>Nd</sub>(0) varies from -9.0 to -8.0, obviously higher than Luochuan loess-paleosols, from -9.3 to -10.4.

The geochemical evidences suggest that the Yili loess is an aeolian deposit and its material source and accumulating environment differs from the Central Loess Plateau.

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## Aliphatic hydrocarbons in the K/T boundary sediments at Kawaruppu, Hokkaido, Japan

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### Introduction

We analyzed aliphatic hydrocarbons in the K/T (Cretaceous/Tertiary) boundary sediments at Kawaruppu, Hokkaido, Japan. And we discussed their distribution patterns in relation to biomass extinction.

### Results and Discussion

Detected aliphatic hydrocarbons were 25 *n*-alkanes from C<sub>12</sub> to C<sub>36</sub>, pristane, phytane, 22 steranes, 17 triterpanes, 62 monocyclic alkanes, 4 bicyclic alkanes, and 11 diamondoid hydrocarbons (adamantanes and diamantanes). They were detected at a concentration level of nmol g<sup>-1</sup> or pmol g<sup>-1</sup>.

Concentrations of all aliphatic hydrocarbons were smaller within the K/T boundary claystone than in the sediments above and below the claystone, which are likely related to the large biomass extinction event at the end of the Cretaceous

Particularly, marked decreases in concentration of longer chain *n*-alkanes (C<sub>27</sub> to C<sub>31</sub>), 5-stigmastane and oleanane within the boundary claystone was likely due to a large devastation of terrestrial plants.

The diastereomer ratios of 5-stigmastanes and 17<sub>21</sub>-30,31-bishomohopanes, and isomer ratios of methyladamantanes and methyladamantanes which have been known as maturity indices, were roughly constant over sedimentary sequence. This indicated that diagenetic effect to these compounds had been nearly constant over the sedimentary sequence.

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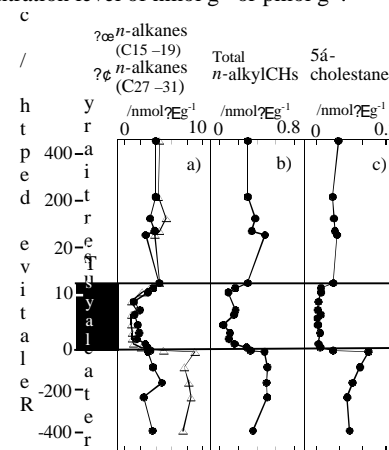


Figure 6. Depth profiles of a) concentrations of *n*-alkanes, b) *n*-alkylcyclohexanes, and c) 5-cholestane in the K/T sediments at Kawaruppu.

## Seasonal variation of $^{231}\text{Pa}$ and $^{230}\text{Th}$ fluxes in the West Caroline Basin

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### Introduction

$^{231}\text{Pa}$  and  $^{230}\text{Th}$  are produced uniformly in seawater from radioactive decay of dissolved uranium isotopes and at the constant activity ratio of 0.093. Both are rapidly adsorbed on settling particles and scavenged from the water column into the underlying sediments.  $^{230}\text{Th}$  is the most particle-reactive. Its flux to the seafloor should approximate its production rate in the water column. These characteristics have led to a wide range of applications as tracers of particle scavenging (Nozaki *et al.*, 1981; Anderson *et al.*, 1983).

### Materials and methods

Sediment trap experiments were carried out in the western equatorial Pacific. Settling particles were collected from the West Caroline Basin by using time-series sediment traps and analyzed for  $^{231}\text{Pa}$  and Th isotopes. Surface sediment samples collected with a multiple core sampler were also analyzed for  $^{231}\text{Pa}$  and Th isotopes. Two sediment traps were deployed at depths of 970 m and 2940 m (1800 m above the bottom) from January to November 1999.

### Results and discussion

The  $^{230}\text{Th}$  concentrations in settling particles ranged from 0.73 to 2.64 dpm/g at 970 m depth and 2.37 to 6.71 dpm/g at 2940 m depth. The  $^{231}\text{Pa}$  concentrations in settling particles ranged from 0.14 to 0.41 dpm/g at 970 m depth and 0.22 to 0.62 dpm/g at 2940 m depth. The flux-weighted mean concentrations of  $^{231}\text{Pa}$  were 0.28 and 0.39 dpm/g at depths of 970 m and 2940 m, respectively. The  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  fluxes showed large seasonal variations, similar to the trend of the total mass fluxes. The maximum  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  fluxes occurred from late February to early March at 970 m depth. Larger  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  fluxes were observed in March and June at 2940 m depth. The scavenging of particle-reactive  $^{230}\text{Th}$  was tied most closely to the flux of organic matter and biogenic opal at 970 m depth and to the flux of carbonate at 2940 m depth in the West Caroline Basin

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## Experimental study on hydrothermal annealing of fission tracks in zircon

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### Introduction

Increasing temperature causes fading of fission tracks (FTs) in minerals. Many annealing experiments were already conducted in atmosphere. On the other hand, mineralogists think that the existence of fluid increases rate of phase change and resolution of crystals. In order to elucidate whether or not the FT annealing at hydrothermal condition is the same as that at atmospheric condition, we performed zircon heating experiments using a hydrothermal synthetic machine.

### Experimental Methods

The zircon grains were shut into platinum capsule with ion exchanged water and heated in Tuttle type reactor. Heating time is 100 hours: 11 hours heating was also performed for preliminary experiments. We performed the experiments at 458 °C ? 611 °C and temperature is constant within ±5°C for 100 hours after reaching plateau. Pressure was kept constant for all experiments as 1000kg/cm<sup>2</sup> (98MPa), equivalent of the crustal depth about 3km.

Observation was conducted according to conventional methods (Yamada *et al.*, 1995a).

### Results and Discussion

For both 11 and 100 hours heating, the track length ? temperature relationships are indistinguishable within 2 standard errors between the present hydrothermal and previous atmospheric annealing data (Yamada *et al.*, 1995b). The relationship between the normalised mean track length and standard deviation of track length distribution is indistinguishable between this and previous studies (Yamada *et al.*, 1995b; Tagami *et al.*, 1998). In addition, the etched shape of confined and 4f<sup>1</sup> surface tracks look similar between the two type of annealing. These lines of evidence suggest that there is no significant differences in track annealing characteristics between the two. It is therefore implied that the annealing kinetics established so far can be applied to thermal history analysis of rocks that were subjected to hydrothermal conditions in nature.

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## The early evolution of the Archean nitrogen biogeochemical cycle

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Nitrogen constitutes essential biomolecules (e.g., nucleic acids, amino acids, and proteins) for sustaining life. The present-day marine N cycle is characterized by a series of oxidation – reduction reactions (e.g., N<sub>2</sub>-fixation, nitrification, and denitrification). These reactions are mediated by a variety of organisms. Gene sequencing revealed that the biological N<sub>2</sub>-fixation has its deep root into the “tree of life”.

To assess the timing of the onset of such processes of N (redox-) cycling in the Earth's history, we determined stable isotopic compositions and contents of organic-N, inorganic-N (clay-N), and organic C of 3.25 - 2.22 billion-year old carbonaceous sedimentary rocks. We analyzed >60 samples of mainly shales from 6 Groups collected in South Africa and Australia, and compared with Phanerozoic shales of various ages.

The distribution pattern and magnitude of N isotopic compositions of the 3.25 Ga black shales and the other Archean–Paleoproterozoic samples are found to be very similar to those of Cretaceous black shales. The N isotopic compositions of organic-N are close to 0 ‰ and those of inorganic-N are positive (~+4 ‰).

As common mechanisms that have controlled marine biogeochemical cycling of N since at least 3.25 billion years ago, we suggest not-mutually-exclusive two mechanisms. One is the microbially mediated redox-cycling of N, involving (possibly cyanobacterial) N<sub>2</sub>-fixation from the atmosphere and denitrification-nitrification in the ancient sedimentary environments. The other mechanism is the microbially mediated non-redox cycling of NH<sub>4</sub><sup>+</sup> between organisms and clays in the ancient sediments. In either case, this study suggests the operation of the microbial N cycling at least since the Mesoarchean. The results of this study are supported by the different data set for other Archean–Paleoproterozoic black shales in Australia (Naraoka *et al.*, in prep).

This study has important implications for the redox evolution of atmosphere and oceans and for the early evolution of the present-day style marine biogeochemical cycling of N.

## A HREE-enriched biogenic ferric redox band in tuffaceous sedimentary rock

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The focus of this study is a redox front generated from a fracture surface in Tertiary tuffaceous sedimentary rock occurring in central Japan. The geological setting and features of the redox front's spatial distribution pattern show that redox reactions have progressed within approximately the last several hundreds of ka, following development of the Quaternary cover's present surface topography. In the sample investigated, the redox band had a width of 17cm and was cut into 17 pieces along the fracture surface. These pieces were analysed by XRF for major and trace elements and by ICP-MS for REEs, to understand the elemental profile from the fracture to the rock matrix. Also, direct examinations with EPMA and SEM-EDS have been carried out to characterise the spatial distribution of elements as well as the microscopic geochemical nature of the front.

The XRF analysis showed that Mn is concentrated in three sharp layers, situated near the fracture surface (less than 20mm). In contrast, the most Fe-concentrated layer was seen from about 50mm from the surface. This strongly suggests that fractionation between Mn and Fe has occurred during front migration. The Mn-concentrated layers also show enrichments of various trace elements such as Zn, Co, Ni, and Ba. On the other hand, the Fe-concentrated layer is characterized by enrichments of P and heavy REEs. The EPMA showed the Fe is distributed heterogeneously in the band and necessarily accompanies P high enrichment. Detailed SEM observation revealed that a fossil microbe colony occurs in the pore space. In places microbial mats with bacterial cells were also identified. Direct examination of the microbial mats with SEM-EDS showed that they are composed of amorphous granules made exclusively of Fe and Si. This suggests that the bacterial activity played an important role in the concentration and fixation of Fe in the redox band under low temperature conditions. Additionally, it is conceivable that the heavy REE enrichment also progressed at the same time. Mass balance calculations were done using the REE analyses of the redox band and the present formation water. If the band formed in the presence of groundwater like that occurring presently, about 10<sup>6</sup> pore-volumes of water would have been required to form the excess REE concentrations in the band.

The implications of these long-term enrichment and fixation processes by biogenic redox front generation at low temperatures will be explored. These implications are relevant to understanding, for example, elemental migration in the global surface weathering system and/or long-term heavy metal fixation for pollutant remediation.

## Extremely low $^3\text{He}/^4\text{He}$ ratios observed in Siberian mantle xenoliths

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To obtain some constraints for the influences of the subducted components, we have analysed noble gas compositions of subcontinental mantle-derived ultramafic xenoliths from Far Eastern Siberia. In the Far Eastern Siberia area, oceanic crusts have been subducting underneath the Eurasian plate since about 100 Ma. Hence, the mantle beneath the Far Eastern Siberia might have been influenced by the components derived from the subducted crustal materials.

By applying both methods of vacuum crushing and stepwise heating for extraction of noble gases, we have revealed the occurrence of  $^3\text{He}/^4\text{He}$  ratios extremely lower than that of MORB in olivine separates for some mantle xenoliths from the Far Eastern Siberia. Since the noble gases were extracted by the crushing method, it would be located mostly in fluid inclusions of minerals. While, MORB-like high  $^3\text{He}/^4\text{He}$  ratios have also been observed for some samples in gases extracted by the crushing method. Hence, at least two kinds of fluid sources with the low  $^3\text{He}/^4\text{He}$  ratio and the MORB-like value should exist in the upper mantle underneath the Far Eastern Siberia area. Furthermore, the orthopyroxene and clinopyroxene of two xenoliths show similar helium compositions to those of olivines. It may indicate that those minerals have trapped the same fluid in fluid inclusions.

The extremely low  $^3\text{He}/^4\text{He}$  ratio in mantle xenoliths requires the occurrence of some mantle source where the He/U ratio should be quite low. However, present sample with an extremely low  $^3\text{He}/^4\text{He}$  ratio does not show low He/U ratio. Since the Far Eastern Siberia area had been located at the subduction zone, occurrence of the extremely low  $^3\text{He}/^4\text{He}$  ratios may have resulted from infiltration of melt related to the old subducted slab.

## Lower crustal renewal associated with formation of sedimentary basins and arc volcanism in the Middle to Late Cenozoic in Japan

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An island arc is a site of active volcanism on the Earth. The successive accretion of island arcs to continental margins is now thought to be the major process of continental growth (Reymer and Schubert, 1978). The process of continental growth through arc magmatism (Yanagi and Yamashita, 1994; Taylor and McLennan, 1995), however, has not yet been made clear. There have been many debates. One of the unknowns is tectonic behaviour of the lower crust. Lower crust delamination and basaltic underplating have often been advocated in relation to the evolution of continental crust (Arndt, and Goldstein, 1989; Bohlen and Mezger, 1989, Kay and Kay, 1991; Rudnick and Fountain, 1995). Both of them seem to have key importance for understanding the unique chemical composition of upper continental crust (Condie, 1993; Wedepohl, 1995; Taylor and McLennan, 1995) and material circulation between the continental crust and the mantle (Doe and Zartman, 1979; Arndt and Goldstein, 1989). Extensive lower crust delamination and basaltic underplating must be reflected on the surface as geologic events such as land subsidence, formation of sedimentary basins, land uplifting and intense volcanic activity.

A marked change in development of sedimentary basins occurred in the Middle Cenozoic in Japan, which had been land until then. Though much different in scale, the back-arc side of Southwest Japan and Northeast Japan underwent the same series of geological events starting from land subsidence through subsequent development of thick sedimentary successions to finally extensive uplifting in association with intense volcanic activity. This series of events may well be accounted for by assuming lower crust erosion and subsequent magma accumulation due to diapiric upwelling in the mantle beneath the sedimentary basins.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of volcanic rocks erupted after the series of events indicate the extensive renewal of the lower crust. Quaternary volcanic rocks erupted in the Miocene sedimentary basins in Northeast and Southwest Japan are low in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (<0.7045) while those erupted on Miocene land areas are high (>0.7045). This suggests the replacement of Cretaceous lower crust by newly formed lower crust beneath the sedimentary basins. The evolution of arc sedimentary basins simultaneously with the intense arc volcanism suggests the generation of arc magma in association with the diapiric upwelling in the arc mantle.

## $^3\text{He}/^4\text{He}$ ratios of fluid samples in Taiwan

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### Introduction

Taiwan is located at a complicated tectonic boundary. Arc-continent collision is ongoing and has generated anomalous geothermal gradients in the Central Range. Hydrothermal activities, hot springs, natural gases are abundant in different tectonic domains. Hence, identification of fluid sources, based on helium isotopic ratios, may provide important information to constrain the magmatic and tectonic evolutions in this area.

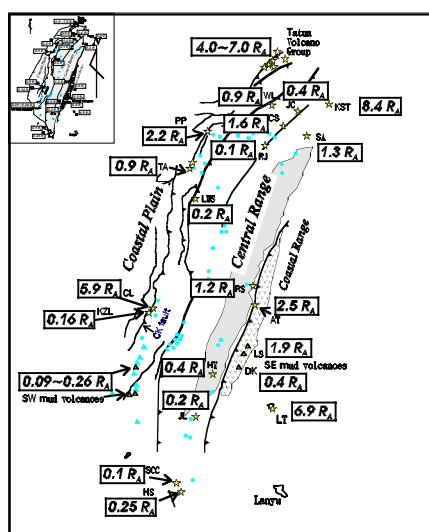


Figure 1: Air corrected  $^3\text{He}/^4\text{He}$  results in Taiwan.

### Discussion and conclusions

According to the tectonic setting, the fluid samples can be divided as three groups with a few exceptions.

- (1) Igneous province: Tatum Volcano Group ( $4.0\sim 7.0R_A$ ), and KST ( $8.4R_A$ ), LT ( $6.9R_A$ ) hot springs are believed magma related in origin. Mantle component ( $8R_A$ ) played an important role in these samples. Samples from other province but close to these areas may have been affected and hence show higher  $^3\text{He}/^4\text{He}$  ratios.
- (2) Central Range province: Most data (WL, JC, RJ, LUS, HY, JL hot springs) range from  $0.1$  to  $0.9R_A$ . This can be well explained by mixing of crustal component ( $<0.1R_A$ ) and air saturated water ( $1.0R_A$ ).
- (3) Coastal Plain province: Expected crustal signatures can be obtained in SW mud volcanoes and KZL hot springs ( $0.1\sim 0.26R_A$ ). This indicates a crustal source was dominant in this area. However, some unusually high ratios were obtained in PP ( $2.2R_A$ ), TA ( $0.9R_A$ ) and CL hot springs ( $5.9R_A$ ) which suggests that the mantle source component also play an important role, although no magma activity has been known in this area since the late Miocene.

## Abnormal enrichment of selenium in Yutangba carbonaceous cherts, Southeast Enshi, Hubei Province, China

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In the carbonaceous cherts at the top of the Lower Permian Maokou Formation limestones at Yutangba, Shuanghe Town, southeast Enshi city, Hubei Province, the element Selenium is so abnormally enriched as to have formed an independent Se deposit, and the main ore type of the Yutangba Se deposit are seleniferous cherts, which constitute the dominant seleniferous layer of the Yutangba Se deposit. The cherts contain as much Se as  $1646 \times 10^{-6}$  on average. In addition, they are rich in organic carbon,  $\text{Al}_2\text{O}_3$ ,  $\text{Si}_2\text{O}$ , but poor in S. In addition to Se, as well as Mo, Cd, V, Co, etc are also highly enriched in the cherts. The chert samples are characterized by low  $\Sigma\text{REE}$ , slight LREE enrichment, relatively heavy Si isotope enrichment, and insignificant variations in  $^{30}\text{Si}$  value within the range of  $1.1\%$   $\sim$   $1.2\%$ . Generally it can be judged from the major element, trace element and REE data and the Si isotopic characteristics that the Yutangba seleniferous cherts were formed in the shallow sea to semi-deep sea anoxic environments and their formation is controlled chiefly by biochemical processes.

We have come to the following conclusions in regard to the mechanism of formation of the Yutangba Se-rich cherts. The Dongwu movement, which had occurred in the late Early Permian, led to the gentle uplift of the crust in the region studied. Owing to the difference in extent of crustal uplifting the relatively closed and stagnant anaerobic conditions were created in the basin. Moreover, the effusion of Emeishan basalts in Southwest China was accompanied with limited sea-floor hydrothermal activities and volcanic eruption. These distal-source magmas and hydrothermal activities brought about large quantities of Si and Se. Under such circumstances the original normally cycling mechanism would necessarily be destroyed and the dynamic balance would be broken, thus leading to vast reproduction of siliceous planktons (mainly plankton plants) to consume the excess Se and Si. Meanwhile, these organisms would die rapidly and be precipitated on the sea floor to form Se-rich carbonaceous cherts.

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## Significance of deep-crustal shear zones in the Southern Granulite Terrain, S. India: New Nd model ages of charnockites

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It has been established that the Archean (>2.5 Ga) high-grade crust of the Southern Granulite Terrain (SGT), south India was subject to intense reworking during the Neoproterozoic (0.75 to 0.5 Ga) along a network of crustal-scale ductile shear belts (Bhaskar Rao et al., 1996; Meissner et al., 2002). The shear belts are well developed along an E-W tract of ~ 350 × 70 km described collectively as the Cauvery Shear Zone (CSZ). Owing to the paucity of age data on granulite domains across the shear belts, their tectonic significance either as crustal sutures, terrane boundaries or merely zones of intracrustal dislocation and loci of recurrent deformation remains enigmatic.

A new database of model depleted mantle ages ( $T_{DM}$ ) for over 80 samples of charnockite gneiss along a N-S corridor encompassing the charnockite highland massifs of Biligiri Rangan (contiguous with the Dharwar Craton), Nilgiri and Kodaikanal, the lowlands of the CSZ and the region east of the Karur-Oddanchatram Shear Zone – KOSZ (Bhaskar Rao et al., 2002) provides a good overview of crust-formation ages in the different domains across the CSZ. Together with multichronometric age data in the literature, the  $T_{DM}$  ages suggest that: (1) the Biligiri Rangan massif consists of the oldest rocks in the SGT with protolith ages for charnockite gneiss up to ~ 3.6 Ga and U-Pb zircon age of ~ 3.4 Ga, (2) the Moyar and Bhavani shear zones represent major Paleoproterozoic terrane boundaries (sutures) between the Biligiri Rangan, the Nilgiri and the CSZ blocks, which yield protolith ages of 3.6 – 3.2 Ga, 2.9 – 2.7 Ga and 3.3 Ga – 3.0 Ga, respectively, consistent with the earlier data summarized by Raith et al. (1999) and (3) the KOSZ, rather than the Palghat-Cauvery shear zone, represents the Archean – Neoproterozoic terrane boundary in the SGT.

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## A melt inclusion study of Baffin Bay picrites

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The primitive nature of Baffin Bay picrites is important in understanding their mantle source components. Previous work identified the former existence of MgO-rich liquids (18 wt% MgO) at temperatures >1425°C (Francis, 1985) with depleted N-MORB-like or enriched E-MORB-like trace element abundances (Robillard, *et al.* 1992).

We have examined major and trace element compositions of homogenised melt inclusions (MIs) in olivine phenocrysts from this suite. Primitive olivine phenocrysts ( $Fo_{85}$ - $Fo_{93}$ ) containing suitable MIs were heated at 1275°C for 6 minutes at  $fO_2=IW+1$  log unit, and then quenched in water. The homogenised MIs were exposed and analysed by EPMA and LA-ICP-MS.

Homogenised MI compositions were corrected for post-entrapment modification (Danyushevsky, *et al.* 2000). The most primitive corrected melt composition contained 21 wt% MgO. Inclusion entrapment temperatures (assuming anhydrous conditions) ranged from 1214 to 1452°C, consistent with Francis (1985).  $CaO/Al_2O_3$  values were mostly 0.80-0.90, although 6 MIs had unusually high values of 0.90-1.1.

For most MIs, Primitive Mantle normalised REE compositions varied from slightly depleted to slightly enriched ( $La/Yb_n=0.53$ -1.96) with flattish M-HREE patterns ( $Eu/Yb_n=0.8$ -1.7). 4-5% of inclusions exhibited striking enrichments in Nb, Ta, Zr and Hf, with La/Nb and Sm/Zr lower than the remainder of the suite, and very low Rb, Ba, Th, Sr and Pb. One of these had  $CaO/Al_2O_3=1.1$ , but trace element data have not yet been obtained from other high Ca/Al MIs.

Projection into Ol-Di-Qz-Jd+CaTs normative space suggests corrected MI compositions could be mixtures of high degree (near cpx-out) partial melts of peridotite generated at  $P \geq 1.2$ GPa and a high Ca/Al (and HFSE/LILE?) component possibly derived from partial melting along an olivine-cpx cotectic.

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## Some clue of coupling relationship between Dongchuan copper and the breakup of Rodinia

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Dongchuan copper ore field locate in Huili-Dongchuan aulacogen which verged on the Sichuan and Yunnan passive continent in china. many geochemical evidences indicate the metallogenic substance is deep phreatic. a)  $\delta^{34}\text{S}$  values are -0.5‰~+16.7‰ the modal value of  $\delta^{34}\text{S}$  is 2‰~11‰.  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values are -0.5‰+16.7‰ b) Most Pb isotope of copper ore are under the natural Pb evolutionary curve, a few sample are up the natural Pb evolutionary curve. c) Co/Ni value of chalcopyrite and pyrite are over 5.0, S/Se value are normal over 500, which Cr, Sn and Ti contents are high. Cobalt pyrite, skutterudite and cobaltite appeared in mineral assemblage, and Co/Au/Pb/Zn/Mo/Sn is reformed during the ore were consumingly superimposed reformed and altered.

By sum up, metallogenic substance is deep phreatic. Some dates (Qiu Huaning et.al.,1997) indicate that metallogenetic epoch of Tangdan deposit was  $712\pm 33\text{Ma}$ - $794\pm 71\text{Ma}$ , which tallies with the breakup of Rodinia. There are many basic volcanic rocks ( gabbro and diabase) and acid rocks (I stype granite), which is Jinning-Chenjiang period (616-1059Ma) (Jiang Jiashen,1998). Those magmas contain many deep phreatic compositions, and time are similar with the breakup of Rodinia, the most important is that copper mineralization were strengthened in the area where magmas emplace. All of those indicate that there are a coupling relationship between Dongchuan copper and the breakup of Rodinia.

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## Isolation of an alkaliphilic metal-reducing bacterium from a saline pond containing high concentrations of boron

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Microbial iron reduction influences biochemical cycles of important elements (e.g., Fe, C, S, P) in natural systems. The purpose of this study was to isolate Fe(III)-reducing bacteria from an extreme environment of high salinity, alkalinity, and boron concentrations.

Enrichments and isolation were performed in a Tris-buffered medium containing sodium chloride, borax and ferric citrate. The isolate, designated as strain 011-A, is a Gram-positive, strict anaerobic rod. Based on the nearly complete 16S rRNA gene sequence analysis, it has 96% similarity with *Alkaliphilus transvallensis*. Profile of phospholipid fatty acids of 011-A indicates predominance of two compounds 16:0 (35.7%) and 16:1w7c (34.2%). The temperature range of strain 011-A was between 10°C and 50°C with an optimal of 30°C. The pH range was between 7.0 and 11.0, with an optimum of 9.5. At pH 9.5, the optimal NaCl concentration for growth was about 2%. Strain 011-A was able to use lactate, acetate, glucose, and hydrogen as alternative electron donors and ferric citrate, ferric-EDTA, Co(III)-EDTA, Cr(VI), and AQDS as sole terminal electron acceptors. Yeast extract (0.025%) was required for growth.

Strain 011-A may represent a novel group of microorganisms, which can reduce a variety of heavy metals at elevated pHs. This isolate may have potential application for bioremediation of metal-contaminated sites. Studies of this bacterium may also expand our understanding of metal reduction in alkaline environments.

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## ***In situ* FTIR study of protonation reactions at the bacteria-water interface**

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Bacterial surfaces are highly reactive and display a strong affinity for metal cations, including heavy metal contaminants and radionuclides. The reactivity of bacterial surfaces arises directly from the presence of proton active organic functional groups on the bacterial cell wall. However, recent experimental studies based on bulk potentiometric titration experiments have reported contradictory results on the types of reactive functional groups on the bacterial surface for identical bacterial species. In order to resolve this disagreement, we have applied a synchrotron-based Fourier Transform Infrared (FTIR) technique to identify and characterize bacterial surface functional groups *in situ* and *in vivo*.

FTIR experiments were performed with the filamentous cyanobacteria *Calothrix sp.*, which form trichomes up to several 100  $\mu\text{m}$  long and are surrounded by a thick sheath (up to 5  $\mu\text{m}$  in thickness). In order to identify the proton active surface sites, IR spectra of individual intact cells and isolated sheath material were collected *in situ* at solution pH values from 3.3 to 9.6. The experiments were carried with a Nic-Plan IR microscope in transmission mode using a Spectra Tech flow through fluid cell with two IR transparent windows (BaF<sub>2</sub> and ZnSe) separated by a Mylar spacer with a path-length of 6  $\mu\text{m}$ . A 0.01 M NaCl electrolyte solution was flowed through the fluid cell at a constant flow rate, and the pH of the input solution was adjusted to the desired pH using 0.1 M HCl and 0.1 M NaOH.

The IR bands of intact *Calothrix* cells display a combination of protein, lipid and carbohydrate functional group peaks. IR spectra from isolated sheaths lack the distinct protein peaks and are dominantly composed of polysaccharide bands in the region between 1200-900  $\text{cm}^{-1}$ . IR measurements of intact cells show a change in peak intensity at  $\sim 1400 \text{ cm}^{-1}$  corresponding to the symmetric vibrational stretching of deprotonated carboxylate functional groups. Identical IR spectra taken with isolated sheaths did not show a change in peak intensity at  $1400 \text{ cm}^{-1}$  suggesting that the reactive carboxyl functional groups are concentrated on the cell wall and not the extracellular polysaccharides. However, a distinct change in peak intensity was detected for the isolated sheaths at  $1238 \text{ cm}^{-1}$  corresponding to P=O asymmetric stretching of  $>\text{PO}_2^-$  phosphodiester functional groups, indicating the presence of proton active phosphoryl sites. This study demonstrates that *in situ* FTIR spectroscopy can be used to identify the reactive functional groups on bacterial surfaces and to investigate the protonation reactions at the bacteria-water interface.

## **Fluid geochemistry of mud volcanoes at the accretionary prism in southern Taiwan**

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Worldwide, most diapiric mud volcanoes are situated at convergence plate-boundaries and are closely related to accretionary wedges. Taiwan, located at the collision belt between the Eurasia plate and the Philippine Sea plate, possesses a typical accretionary wedge and has developed numerous mud volcanoes both on-land and offshore. The gases from most mud volcanoes in Taiwan are mainly CH<sub>4</sub> (>90%) with minor N<sub>2</sub> and CO<sub>2</sub> content. Available helium isotopic data demonstrate the gases are dominated by crustal components, although some samples showed mantle-derived gas signatures. To better understand the evolution of mud volcanoes at the developing accretionary prism, fluid compositions from various mud volcanoes in different tectonic environments of southern Taiwan were compared.

Fluid samples of representative mud volcanoes from three tectonic settings in southern Taiwan were collected for geochemical analysis. The principal component method was utilized to evaluate potential factors affecting chemical variations. Preliminary results show that two factors explain 78% and 16%, respectively, of the observed chemical variation of the fluid samples. Factor F1 controls most of Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> variations in the fluids and is considered to be mainly the contribution of marine sedimentary pore water. The F2 factor affects mainly SO<sub>4</sub><sup>2-</sup> concentrations, which may be a result of meteoric water addition, although the amount is generally small.

Mud volcanoes in southern Taiwan can be divided into two categories based on their fluid geochemistry. The mud-volcano fluids from the foreland basin show more F1 contribution than those from the hinterlands. This suggests that fluids from the hinterlands may have undergone a higher grade of diagenesis and hence exhibit more signature resulting from water-rock reaction and dehydration of clay minerals. Another alternative is that deeper thrusts may exist in the hinterland, which consequently could provide a pathway for deep dehydration water addition.

## Petrographic and Geochemical Evidences indicating the crustal assimilation in the within-plate basalts: Karasar Basalt (Divri\_i-Sivas, Central Anatolia, Turkey

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Karasar basalt outcropping as the thick bedded lava flows can be divided into two groups according its textural features: First group basalts have a holocrystalline-intersertal texture while second group has a holocrystalline porphyric texture. Quartz xenocrysts surrounded by epitaxitic clinopyroxene microlithes have been observed in the second group basalts. Biotite minerals in the groundmass of the some basalts belonging to second group have also been observed.

First group basalts have ranging from 50% to 54 %SiO<sub>2</sub>, 1.11-1.38 %K<sub>2</sub>O and 30-42 ppm Rb while second group basalts have 45% to 48 %SiO<sub>2</sub>, 0.52-0.76 % K<sub>2</sub>O and 21-28 ppm Rb. All the samples of the Karasar basalt have an alkaline character. Trace element data show that the Karasar basalt indicate the within-plate character.

On the basis of the petrographical and geochemical characteristics of the Karasar basalt, such a model can be proposed for the evolution: An alkaline magma was generated by the low degree partial melting of the lherzolitic upper mantle material. While this magma rises in the cracks developed during the Neotectonic period in the thickened continental crust, first lava flows was enriched in Si, K and Rb by crustal assimilation, and later lava flows were uncontaminated or little contaminated.

## <sup>182</sup>Hf-<sup>182</sup>W in meteorites and the timescale for planetary formation

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Determining the chronology according to which planetary bodies were assembled in the early Solar System is essential for a better understanding of star- and planet-forming processes. Astronomical observations place severe constraints on the formation time of gas-giant planets (possibly with a solid core of ten Earth masses) to within a few million years after central star formation and before complete dissipation of nebular gases. Formation of terrestrial planets before the nebular gas dissipation is also consistent with the observed solar He and Ne components incorporated into the Earth's mantle during the magma ocean epoch. The standard model of planet formation predicts that Mars-sized bodies will form within 0.1 Ma of the origin of the Solar System. Various chronometers have been used to determine that basaltic lava flows on the surface of Vesta formed within 3 Ma of the origin of the Solar System. A major challenge to such a short timescale is that some published Hf-W isotopic data require a very long duration (60<sup>+4500/-10</sup> Ma) for the formation of the terrestrial planets (Lee and Halliday, 1996). The Hf-W data for eucrites, if compared to the currently accepted high initial solar value of <sup>182</sup>Hf/<sup>180</sup>Hf = 2.75x10<sup>-4</sup> (Lee and Halliday, 2000), indicate a late formation of Vesta at 16 Ma (Quitté et al., 2000), inconsistent with live <sup>53</sup>Mn and <sup>26</sup>Al in eucrites. Such a long timescale, if correct, calls into question our understanding of the main growth stage of planet formation. Our new Hf-W data (Yin et al., 2002) show that the solar initial <sup>182</sup>Hf/<sup>180</sup>Hf = 1.00x10<sup>-4</sup>, substantially lower than the accepted higher value. Furthermore, ε<sub>w</sub> for chondrites is ~2 ε-units lower than that of the Silicate Earth. We show that the main growth stage (63%) for the Earth is largely completed in ~10 Ma, and the Moon-forming giant impact is dated at 29 Ma. Our new data also resolve the inconsistency between Hf-W, Mn-Cr and Al-Mg chronologies for eucrites and support a very short timescale (< 3 Ma) for formation and melting of Vesta.

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## Extension of the Afar Plume Material: He isotope Constraints

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Afar plume triggered the activities of Oligocene to recent Afro-Arabian volcanism. We have investigated <sup>3</sup>He/<sup>4</sup>He and revealed a contribution of plume component in Ethiopian lavas. Ebinger and Sleep (1998) recently suggested that volcanisms in northern and central Africa during this epoch were results of single large heat source, Afar Plume. Herein we report helium isotopic compositions of olivine phenocrysts in lavas and xenoliths of Yemen and Saudi Arabia on north east, and Hogger and Kivu west and southward respectively to investigate the extension of the plume component.

### Results and Implications

<sup>3</sup>He/<sup>4</sup>He ratio of olivine phenocrysts from Kivu, Saudi Arabia, Hogger lavas varies between 2.3 Ra with evidence of radiogenic <sup>4</sup>He addition, and 8.9 Ra. Thus it is unlikely to account an inheritance of primitive deep signature. Another important feature is the relative depletion of magmatic He in these lavas comparing to those showing high <sup>3</sup>He/<sup>4</sup>He in Ethiopia. This implies that the lower <sup>3</sup>He/<sup>4</sup>He observed in distant localities were not a result of dilution by additional radiogenic <sup>4</sup>He of originally Afar-type component.

In Yemen we observed clear plume signature in olivine phenocryst of one sample (16.2 Ra). Diopside from metasomatic vein in the composite xenolith showed higher <sup>3</sup>He/<sup>4</sup>He ratio comparing to non-metasomatic olivine. The metasomatic agent was reported to have trace element characteristics identical to Afar plume. Our results indicate that the metasomatic agent was in fact of plume-origin. Therefore, it is evident that plume originated metasomatism affected the lithospheric mantle beneath Yemen. Revealing to what lateral extent the metasomatism occurred will be another clue to whether or not an enormous plume exists. It is then noteworthy that mantle xenoliths from Sidamo, Ethiopia, are anhydrous and show no evidence of metasomatism.

Distant localities show no evidence for the contribution of plume component, thus limited extension of Afar plume component is suggested.

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## Mantle metasomatism and rapid ascent of slab components beneath Miyakejima volcano, Izu arc, Japan

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<sup>238</sup>U-<sup>230</sup>Th-<sup>226</sup>Ra systematics of Miyakejima volcano is shown together with major and trace element compositions as well as their Sr-Nd-Pb isotopes to estimate the timescale of magmatic processes beneath island arc. Based on previous geological works, we divided the volcanic history of Miyakejima into four stages. Strong enrichment of LILE compared to HFSE, and Sr-Nd-Pb isotopic systematics observed imply metasomatism of depleted mantle by fluid related processes with little contribution from a sedimentary component. The variations of some trace element ratios (e.g. U/Th, B/Nb, and Ba/Th) are made by this process.

<sup>238</sup>U-<sup>230</sup>Th disequilibrium observed in Miyakejima lavas ((<sup>238</sup>U/<sup>230</sup>Th)=1.2-1.5) also implies metasomatism of depleted mantle by fluid related processes occurred within the last 350 kyr. In the equiline diagram, trends of Stage 1 and 2 are regarded as two different isochrones that have common initial (<sup>230</sup>Th/<sup>232</sup>Th) ratio. Our model regarding slab dehydration suggests that the fluid released from the slab can contain a certain amount of Th, resulting in that apparent <sup>238</sup>U-<sup>230</sup>Th age calculated does not represent absolute time of material transport in the mantle wedge. However, the differences of the age between each stage, 15 kyr between Stage 1-2, and 3 kyr between Stage 2-3, are valid and they should be the interval of individual fluid-release.

Very large <sup>226</sup>Ra-<sup>230</sup>Th disequilibrium ((<sup>226</sup>Ra/<sup>230</sup>Th)>2) observed in some lavas suggests actual transport time of slab component in the mantle wedge as short as a few kyr, corresponding to ~50-100 m/yr of the ascending rate of slab materials to the surface. Such a rapid rate can be achieved by material transport via crack system in the mantle wedge explained by hydrofracture model and channel-flow model, rather than permeable-flow model.

From the <sup>226</sup>Ra-<sup>230</sup>Th disequilibrium in Stage 3 lavas, the minimum interval of the fluid-release is calculated as ~1 kyr. Therefore, the fluid-release and subsequent melt generation in the mantle wedge are episodic events that intermittently occur with 1~15-kyr scale, indicating that subduction zone volcanism is generally controlled by the timing of the fluid-release from the slab occurring within several-kyr scale.

In contrast, Stage 3 and 4 samples depict a mixing trend in the equiline diagram between old andesitic magma and newly injected less-differentiated magma. The involvement of less-differentiated magma generally decreases from Stage 3 towards present. Stage 1 magma is a primary end-component of the andesitic magma which differentiated >7 kyr in the magma chamber that is isolated in the crust after active eruptions of Stage 1.

## Extractions of *in-situ* produced $^{14}\text{C}$ in terrestrial quartz and measurements of $^{14}\text{C}$ production rate using saturated quartz

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The measurement of cosmic-ray-produced  $^{10}\text{Be}$  and  $^{26}\text{Al}$  in quartz exposed at the Earth's surface has enabled numerous scientific investigations aimed at quantifying landscape evolution. We are establishing a reliable measurement system for *in-situ* produced  $^{14}\text{C}$  ( $t_{1/2}=5,730$  yr) extraction from quartz, based on step heating of powdered quartz samples to 500-1550°C under flowing carrier gas in a tube furnace. The background of the current extraction system is  $(2-5)\times 10^5$  atoms  $^{14}\text{C}$  using deeply shielded quartz from Homestake mine. This is comparable to the background level reported by Lifton *et al.*, (2001) using their "Dry extraction" method. The recovery yield of carrier gas is >95%.

To obtain the production rate of *in-situ* produced  $^{14}\text{C}$  in quartz, we measured  $^{14}\text{C}$  in purified quartz from the Beacon sandstone collected from the Transantarctic Mountains, Antarctica. Since  $^{10}\text{Be}$  and  $^{26}\text{Al}$  concentrations in aliquot of samples were nearly saturated, the erosion rates of these samples were less than a few mm/ $10^4$  yr. *In-situ* produced  $^{14}\text{C}$  in the quartz, therefore, is saturated implying that observed  $^{14}\text{C}$  activity in the quartz sample is equal to the production rate of  $^{14}\text{C}$  in the quartz for the  $^{14}\text{C}$  mean-life. This is the most direct and unambiguous method to obtain the production rate of a radionuclide.

The preliminary result is  $(8.2\pm 0.5)\times 10^5$  atom  $^{14}\text{C}/\text{g SiO}_2$  compared to  $(6.4\pm 0.1)\times 10^7$  atom  $^{10}\text{Be}$  and  $(2.2\pm 0.1)\times 10^8$  atom  $^{26}\text{Al}/\text{g SiO}_2$  respectively. The preliminary  $^{14}\text{C}/^{10}\text{Be}$  and  $^{14}\text{C}/^{26}\text{Al}$  production rate ratios at the high elevation site are 2.4 and 0.4, respectively.

Comparison of our preliminary results for  $^{14}\text{C}$  in saturated Antarctic rocks and the most recent estimate of the production rate from Lifton *et al* (2001) indicates that our *in-situ* produced  $^{14}\text{C}$  extraction efficiency from quartz is greater than 94%.

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## A redox front migration process in sedimentary rock- Long-term behavior of nuclide migration relevant to near-field processes in radioactive waste disposal -

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The development of redox fronts in geological environments, e.g. in the near- and far-fields of high level radioactive waste (HLW) repositories of all designs, will be unavoidable. The long-term behaviour of redox front migration, therefore, is one of the key processes to evaluate the barrier function of the near-field geological environment.

As an analogous example of long-term redox front migration, investigations have been carried out on a redox front generated up to several meters below the ground surface in Tertiary sedimentary rock occurring in central Japan. The geological setting and features of the redox front's spatial distribution pattern show that redox reactions have progressed within approximately the last several hundreds of ka, following development of the present surface topography of the Quaternary cover. Detailed microscopic observations and geochemical analysis by XRF, EPMA, ICP-MS and SEM-EDS show that the redox front has accumulated concentrations of major and minor elements that are at least several times more than the background levels. Particularly, transition elements such as Zn, Co and Ni as well as HREE are co-precipitated within a band where Fe and Mn oxide are concentrated at the front. Microscopically, aggregations of spheroidal amorphous ferric iron grains with diameters of a few micrometers are identified in the pore spaces of the sedimentary rock. This suggests that the migration of the redox front might occur at the same time as these amorphous iron oxide grains move through the rock matrix scavenging the dissolved elements during their migration, probably due to their high effective surface area which is available for ionic adsorption. Such a process could also be effective for radionuclide retardation in the near field environment. The profile of ratios of ferrous to ferric iron, from the oxidising part to the reducing part through the front, also reveals that the oxidised part of the host rock has slightly recovered its reducing environment after the redox front has passed. This is suggested by the supply of reducing pore water through the surface organic rich soil, and the mobile morphological feature of oxidants might also be considered as a reason for redox front movement.

The front is considered a long-term analogue for a geochemical process expected to occur in the sedimentary rock that might occupy the near-field environment of a future HLW repository.

## A kinetic experiments of oxidation of arsenopyrite in $\text{Fe}_2(\text{SO}_4)_3$ solutions

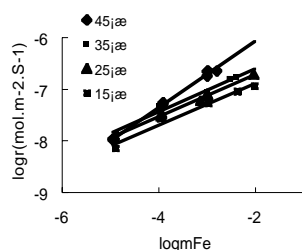
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Arsenopyrite is a moderately stable mineral and it can stably exist only in strongly alkaline and reducing environments. Oxygen-rich, acidic surface waters are favorable to the oxidation and dissolution of arsenopyrite and the release of As, Fe and S from it.

In this paper kinetic experiments were made on the oxidation of arsenopyrite in  $\text{Fe}_2(\text{SO}_4)_3$  solutions (pH=1.8) with a concentration of  $110^{-2}$ — $110^{-5}$  mol.kg<sup>-1</sup> at the temperatures of 45°C, 35°C, 25°C and 15°C in a mixed flow reactor.

The results have shown that the rates of oxidation of arsenopyrite increase with increasing concentrations of  $\text{Fe}_2(\text{SO}_4)_3$  solutions and the rise of reaction temperature as shown in the Figure;



Arsenic released during oxidation of arsenopyrite is present dominantly as hydrous compounds of As(III); As(V) is present in subordinate concentrations and is derived mainly from the outermost layer of oxidized arsenopyrite at the beginning of an experiment while As(III) is the product of oxidation of arsenopyrite. In  $\text{Fe}_2(\text{SO}_4)_3$  solutions the oxidation of As(III) to As(V) proceeds very slowly allowing As(III) to predominate in the solution. The stability of As(III) tends to increase with decreasing oxidant concentration and increasing reaction temperature;

The existence of  $\text{Cl}^-$  in the solutions is favorable to the oxidation of arsenopyrite and the acceleration of conversion of As(III) to As(V).

### References

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## X-ray Study of Actinide Host-Phases Formation

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Crystalline phases with fluorite-derived structure (zirconolite, pyrochlore) are the promising hosts for long-lived actinide immobilization. These waste forms are usually produced by solid state synthesis – cold pressing at 100-200 MPa followed by sintering at 1300 – 1500 °C for 3-4 hours (CPS). Duration of synthesis required for a single-phase product fabrication depends on chemical composition of the target host-phase. In order to determine optimal parameters of CPS method of actinide waste forms fabrication we have studied rate of phase formation in four systems of different composition: Ca-Zr-Ti-O (the target phase is zirconolite,  $\text{CaZrTi}_2\text{O}_7$ ); Ca-Ce-Ti-O (pyrochlore,  $\text{CaCeTi}_2\text{O}_7$ ); Gd-Ti-O (pyrochlore,  $\text{Gd}_2\text{Ti}_2\text{O}_7$ ), and Gd-Zr-O (pyrochlore,  $\text{Gd}_2\text{Zr}_2\text{O}_7$ ). Synthesis was performed using initial oxide precursor powdered up to grains dimension of about 20 μm. Runs were carried out in air or pure oxygen (for Ce-batch only) in temperature range from 800 to 1600 °C and period of sintering from 5 to 100 hours. Products of the experiments were examined using XRD analysis. The rate of target phase formation is the fastest in titanate systems (Ca-Ce-Ti-O and Gd-Ti-O) and the lowest in the Gd-Zr-O system. Rate of zirconolite formation has intermediate value. Formation of titanate pyrochlore-based matrix takes 3-4 hours at 1400 °C and 0.5-1 hour at 1500 °C. To obtain the single phase zirconate pyrochlore for actinide immobilization too long time of sintering exceeding 40 hours at 1600 °C is required. Zirconate-based pyrochlore is a promising waste forms due to its very high chemical durability and stability to radiation damages induced by α-decay events. To produce this matrix some other methods may be employed instead of the CPS route, for example inductive melting in a cold crucible or self-sustaining high-temperature synthesis.