

## Enriched mantle source for the Cretaceous alkaline lamprophyres from the Catalonian Coastal Ranges (NE Spain)

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During the Cretaceous, the opening of the Bay of Biscay led to a widespread alkaline magmatism in northeast Iberia [1]. This magmatism is recognised in the Pyrenees [2] and in the Catalonian Coastal Ranges [3]. In the latter sector, it is represented by lamprophyre sills, classified as camptonites. They are hypocristalline porphyritic rocks composed of large mafic crystals (clinopyroxene, kaersutite, olivine pseudomorphs and opaque minerals) set in a fine-grained groundmass. Most of the groundmass consists of microlites of feldspars and kaersutite; apatite is a common accessory phase.

The lamprophyres are basic and ultrabasic rocks enriched in incompatible elements (10 to more than 100 times over the primitive mantle). They show a Ti/V ratio over 50, similar to OIB-type rocks. In order to obtain petrogenetic information from the incompatible trace elements, only the most primitive samples (MgO > 7 wt. %) were considered. In addition, rocks with high volume fractions of large crystals were dismissed as their composition is strongly influenced by the accumulation of the crystals [4].

The primitive mantle-normalised multi-element patterns are very similar to each other, suggesting a common magma source. (La/Lu)<sub>N</sub> values (14.9-17.3) indicate highly fractionated patterns. All the samples show positive anomalies for Nb-Ta and smaller ones for Ba; some of the samples also present a negative anomaly in Pb. These data point to an asthenospheric enriched mantle source similar to EM-1 [5]. Small differences are observed for K, which correlate with the proportion of kaersutite in the samples. Slight differences in P are probably related to the presence of apatite.

The εSr values define a wide variation range (-11.7 to +14.9). Given that these variations do not correlate with the SiO<sub>2</sub>, MgO or Sr contents, crustal contamination can be ruled out. Therefore, a heterogeneous mantle source is inferred, as previously reported for the Permian and Triassic magmatisms in the Pyrenees [6].

In contrast, the εNd values (+3.1 to +4.4) and the Pb isotopic ratios (<sup>206</sup>Pb/<sup>204</sup>Pb: 19.06–19.46; <sup>207</sup>Pb/<sup>204</sup>Pb: 15.65–15.70; <sup>208</sup>Pb/<sup>204</sup>Pb: 39.28–39.82) show small variations. The low Pb ratios discard the involvement of a HIMU-type component. The Sr-Nd-Pb isotopic values support a heterogeneous, asthenospheric mantle source with the involvement of an EM-1 component [5].

The obtained T<sub>DM</sub> ages are very consistent (0.55-0.60 Ga). They may reflect a Cadomian fractionation event in the mantle.

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## Photodissociation origin of Archean S-MIF and dynamical sulfur cycling under highly reducing atmosphere

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Mass-independent fractionation of sulfur isotopes (S-MIF) demonstrated that Earth's atmosphere was virtually oxygen-free in the Archean [1], and is a key to understand chemistry of atmosphere and ocean before the rise of oxygen. However, the mechanism and factor controlling the S-MIF signal have been poorly understood yet. We newly determined higher resolution UV absorption cross sections of not only <sup>32</sup>SO<sub>2</sub>, <sup>33</sup>SO<sub>2</sub> and <sup>34</sup>SO<sub>2</sub> but also <sup>36</sup>SO<sub>2</sub> within the two absorption bands: (1) 190 – 220 nm and (2) 250 – 320 nm. These data together with chemical reaction model allow us to predict isotopic compositions of photochemical product. The calculated photochemical fractionation pattern assuming broadband solar UV flux reproduce our previous work [2], though the effect of UV shielding by each atmospheric species including SO<sub>2</sub> itself differ from previously estimated trend. Nonetheless, almost all of the simulations result in Δ<sup>36</sup>S/Δ<sup>33</sup>S ratio of -0.9 ~ -1.1, generally reproducing those observed in Archean sedimentary rocks. Thus, we conclude that photodissociation of SO<sub>2</sub> was a primary MIF-yielding reaction in the Archean atmosphere. Our simulation predict, however, the remaining SO<sub>2</sub> after UV photolysis acquires positive Δ<sup>33</sup>S as opposed to widely-accepted previous model where H<sub>2</sub>SO<sub>4</sub> (-Δ<sup>33</sup>S) and S<sub>8</sub> (+Δ<sup>33</sup>S) aerosols carried "opposite" MIF signals into ocean and sediment [4,5]. We speculate the possibility that almost Archean sulfide deposits were produced by sulfate reduction. The new model requires relatively inert reducing form of sulfur reservoir. If the atmosphere was strongly reducing and contained high level of CO or CH<sub>4</sub>, photolytically produced SO was finally transferred into OCS [2] or organo-sulfur compounds [6], respectively, which remained in the atmosphere and were not readily converted into sulfide. Occasional oxidation of the reducing sulfur pool enhanced sulfate concentration and deposited rare sulfate minerals with negative Δ<sup>33</sup>S. The new dynamical sulfur cycle model may explain observed heterogeneity of S-MIF records in the basin to microscopic scale. If correct, this implies more reducing Archean atmosphere than previously thought.

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## Petrological Exploration of podiform chromitite by using of detrital spinel, Sangun Zone, southwest Japan.

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### Sangun zone ultramafic rocks and chromitite

Many ultramafic complexes some of which have chromitite bodies are exposed in the Sangun zone in central Chugoku district, Southwest Japan. All complexes are harzburgite-dominant, and dunite is various in amount on each complex and sometimes has small amounts of chromitite in it [1]. A chromitite pod is always enclosed by dunite envelopes and large chromitite bodies are exclusively found in relatively dunite-dominant complexes or portions [1, 2]. Largest chromite mines of Japan that are Wakamatsu and Hirose are exists in the northern part of Tari-Misaka complex.

### Detrital chromian spinel as a tool for exploration of podiform chromitite

Exploration of podiform chromitite has been difficult, because its occurrence is usually very irregular in ultramafic complex. Matsumoto and Arai (1997) proposed the petrological exploration of podiform chromitite by using of spinel chemistry and morphology from the rocks from the outcrops [2, 3]. Above study is epoch-making as an investigating method for exploration of podiform chromitite. However, an investigation precision does not go up by this Method. Because it dose not have the good exposure of ultramafic rocks in the Sangun zone. In this research, we observed detrital spinel in bottom sediment of small creek in and around the ultramafic complex. By this method, there is an advantage that can analyze much spinel grain at once. Moreover, it is expected that we can evaluate a large locality (complex) with a comparatively sufficient precision.

Cr# (Cr/Cr+Al) of detrital chromian spinels from the creek around relatively dunite rich ultramafic complex varies from 0.55 to 0.65. In contract to this, from the creek around dunite free or poor ultramafic complex, Cr# of detrital chromian spinels varies from 0.40 to 0.60. And complex with relatively large chromitite show high in Cr# and Mg# ( $Mg / (Mg+Fe^{2+})$ ) of chromian spinel. Above results are basically same as Matsumoto and Arai (1997). However, it is very significant results for exploration of chromitite that we have calculated the quantitative chromitite's existence rate each ultramafic complex separately. That is northern part of Tari-Misaka complex is the place where most high potentiality of chromitite deposit. This result also concordant with the idea of chromitite formation proses [4, 5].

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[2] Matsumoto & Arai (1997) *Resource Geology* **47**, 189-199.

[3] Matsumoto & Arai (2001) *Mineralogy and Petrology* **73**, 305-323.

[4] Arai & Yurimoto (1994) *Economic Geology* **89**, 1279-1288.

[5] Zhou *et al.* (1994) *Mineral. Deposita* **29**, 98-101.

## Microbial characterization at iron-clay interfaces after 10 years of interaction *in situ* in an argillaceous formation (Tournemire, France)

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### Introduction

Microbial activity has been proven to occur in argillaceous formations, as well as the development of exogenous microorganisms within disturbed areas [1]. In the context of a geological disposal of radioactive waste in clayey formations, the consequences of such a microbial activity are of concern regarding the corrosion of metallic materials. In particular, sulfate- or thiosulfate-reducing bacteria may influence localised corrosion processes [2], that may lead to a premature loss of watertightness of containers. Moreover, the passive film, which is formed progressively during the generalised corrosion process and induces a decrease of corrosion rates, may react with iron-reducing bacteria which could thus promote corrosion [3]. The purpose of the present work was to characterise the microbial diversity that may have impacted corrosion processes at the interface between re-compacted argillite and steel coupons after 10 years of interaction under *in situ* conditions inside the Toarcian argillite layer in Tournemire (France).

### Results and Conclusion

The characterization of the microbial diversity was carried out using 16S rRNA genes cloning and culture media. More than 630 clone sequences were analyzed and 123 isolates were identified. Altogether, 19 phylotypes and 55 taxa were defined. They were affiliated to only 3 bacterial phyla: *Firmicutes*, *Actinobacteria* and *Proteobacteria*. The biodiversity identified differs depending on the steel type and the location of the sample, indicating the influence of *in situ* physico-chemical conditions. Moreover, isolates and clone sequences have revealed that sulfate-reducing bacteria, iron-reducing bacteria as well as thermotolerant strains able to grow at temperatures up to 75°C could develop in this environment. Different microbial populations can colonize the interfaces between materials in a very short period of time compared with the timescales of a geological disposal. These results should be considered to assess the consequences of microbial activities on the evolution of the metallic disposal components.

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## Evidence from D/H and volatile abundances of impact melts for a surficial water reservoir on Mars

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Martian surface morphology implies that persistent liquid water once existed on its surface and played a significant role in the formation of weathered regolith. In order to study this surficial water we measured volatile abundances (H<sub>2</sub>O, CO<sub>2</sub>, S, Cl, F) and H isotopes of impact melts (IMs) and maskelynite (shocked plagioclase) in geochemically enriched (LAR 06319 [LAR06]) and intermediate (EETA79001 [EETA79]) shergottites by ion microprobe analysis. Early studies of inert gases contained in IMs from EETA79 match the relative abundances of modern Martian atmosphere.

IMs in LAR06 contain lower H<sub>2</sub>O (~150ppm), CO<sub>2</sub> (~20ppm) and S (100-400ppm) but higher F (10-30ppm) and Cl (40-80ppm) than IMs in EETA79 (~300ppm H<sub>2</sub>O, ~300ppm CO<sub>2</sub>, 3200ppm S, <3ppm F, ~30ppm Cl). The major element compositions of IMs are probably derived by partial melting of primary plagioclase and pyroxene. Likewise, the halogen abundances could possibly reflect the incorporation of primary phosphates. On the other hand, the much higher H<sub>2</sub>O/CO<sub>2</sub> ratios than that of the Martian atmosphere (<10<sup>-3</sup>) imply the presence of another water source.

In a previous study [1] based on olivine-hosted melt inclusions we showed that the primary magma of the geochemically depleted shergottite (Yamato 980459 [Y98]) had a chondritic low- $\delta$ D value of 275‰, whereas that of LAR06 had a very high- $\delta$ D value of 5079‰. In contrast with such extreme  $\delta$ D differences, matrix phases in Y98 and LAR06 both have moderate  $\delta$ D values. Groundmass glasses (GGs) in Y98 exhibit a slightly greater  $\delta$ D variation of 200-1600‰, but still much less extreme than the range exhibited by the melt inclusions. The  $\delta$ D values of the Y98 GGs rise with increasing water contents, implying mixing of two components: near-surface moderate- $\delta$ D and magmatic low- $\delta$ D components. On the other hand, IMs and maskelynites in LAR06 exhibit lower  $\delta$ D values of ~1000-3000‰ than the primary LAR06 melt (5079‰), although mixing calculations suggest that these matrix  $\delta$ D values could have been modified by contamination of <30ppm terrestrial water ( $\delta$ D~-200‰). IMs in EETA79 also have a moderate  $\delta$ D value of ~1600‰.

This study shows that the matrix phases (GG, IM and maskelynite) in all three shergottites have a relatively limited range of  $\delta$ D values regardless of the distinct  $\delta$ D of their magmatic sources. A [ $\delta$ D vs. 1/H<sub>2</sub>O] mixing diagram shows a convergence among the matrix  $\delta$ D values, which could be attributable to the impact-induced addition of a common near-surface water with a moderate  $\delta$ D value (~1200-2000‰). The origin of this surficial water reservoir remains unresolved: (1) it may be derived from the Martian atmosphere, but its moderate  $\delta$ D values are distinctly lower than the widely-accepted atmospheric  $\delta$ D value of ~4000-5000‰, and/or (2) it could originate from the addition of a weathered soil/dust component enriched in volatile elements. [1] Usui *et al.* (2012) *43rd LPSC*, #1341.

## Natural variations of uranium isotopes in uranium ore minerals

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### Introduction

Recent studies have shown significant variations in <sup>235</sup>U/<sup>238</sup>U and <sup>234</sup>U/<sup>238</sup>U ratios in geologic materials. We have investigated the uranium isotopic compositions of natural ores from various uranium deposit types with the use of MC-ICP-MS to better understand mechanisms and processes for fractionation of uranium isotopes in different geologic conditions.

### Results

The  $\delta^{235}\text{U}$  and  $\delta^{234}\text{U}$  values of uranium minerals from various types of deposits worldwide show variations of 1.8 and 500‰, respectively, measured relative to NBL CRM 129-A. Higher  $\delta^{235}\text{U}$  values are generally recorded by magmatic- or metasomatic-related U mineralization or deposits that have igneous rocks as a source of uranium (Fig. 1). High-grade unconformity type deposits have  $\delta^{235}\text{U}$  values around -0.9‰. Vein-type, sandstone-hosted, most unconformity-type deposits, and uranium mineralization in the Beaverlodge area have lower  $\delta^{235}\text{U}$  values (Fig. 1).  $\delta^{234}\text{U}$  values for most samples analyzed are around 30‰ and record secular equilibrium. Some samples have  $\delta^{234}\text{U}$  values much lower or higher than 30‰ associated with addition or removal of <sup>234</sup>U during the past 500 Ka.

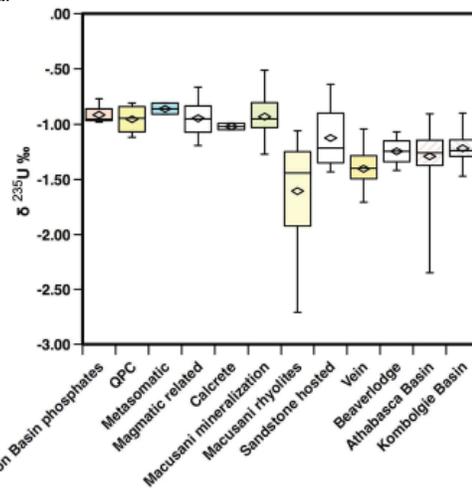


Figure 1:  $\delta^{235}\text{U}$  values for studied samples

### Discussion

The  $\delta^{235}\text{U}$  and  $\delta^{234}\text{U}$  values recorded in uranium ores from different types of deposits indicate that there are at least two different mechanisms responsible for <sup>235</sup>U/<sup>238</sup>U and <sup>234</sup>U/<sup>238</sup>U fractionation. <sup>234</sup>U/<sup>238</sup>U disequilibria ratios indicate fluid alteration of the uranium minerals or rocks and postdepositional migration of <sup>234</sup>U. Fractionation of <sup>235</sup>U and <sup>238</sup>U as a result of nuclear volume effects results in enrichment of the heavy isotope in reduced insoluble species relative to oxidized mobile species. Therefore, isotopic fractionation effects should be reflected in <sup>235</sup>U/<sup>238</sup>U ratios in U ore minerals formed either by reduction of U<sup>6+</sup> to UO<sub>2</sub> or chemical precipitation in the form of U<sup>6+</sup> minerals.  $\delta^{235}\text{U}$  values of uranium ore minerals from a variety of deposits are controlled by isotopic signature of the U source, the efficiency of U precipitation, and later fluid-produced alteration of the ore.

# Climate extremes and volcanic eruptions: Trace elements, isotopes and U-series geochronology recorded by a <sup>1</sup>Late Quaternary stalagmite

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Documenting the timing of large volcanic eruptions is critical in climate change research because volcanic gas and ash spreading globally from equatorial eruptions can cause a significant change in global temperatures [1,2,3,4]. Cave carbonate deposits provide an unprecedented opportunity to reconstruct climate changes, volcanic eruptions, and recurrence patterns of paleo-seismic events [5]. Through high-precision U-series dating and micro-chemical analysis, speleothems are capable of providing tandem records of climate and environmental change, and thus can offer new insights into the complex interplay of seismic, volcanic and hydrological processes.

We investigated a stalagmite sample from a cave in a volcanically active region in Indonesia by a high-resolution micro-sampling, high-precision U-series dating combined with trace element, C, O, and Sr isotope analysis. The stalagmite contains several dark laminas that record major volcanic eruption cycles and/or episodic climatic shifts. A sharp increase in the trace element abundance, which correlates clearly with increasing  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values and a drop in  $^{87}\text{Sr}/^{86}\text{Sr}$  values, is conspicuous in the black layers. Strikingly, the pattern of  $^{87}\text{Sr}/^{86}\text{Sr}$  values of the investigated stalagmite sample parallels their U/Th age spectra. Voluminous  $\text{CO}_2$  emission due to phreatic eruptions and/or a sudden turnover to dry climate episodes are interpreted as leading to carbonate growth hiatuses before the precipitations of black layers. More future studies of millimetre to submillimetre-scale geochemical investigations and precise age dating of speleothems from volcanically active regions will provide detailed insight into interplay among volcanic cycles, fluid flow events and climate changes.

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