

## Fe isotope fractionation during Fe(III) hydrolysis in Cl<sup>-</sup> medium at low temperatures

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Realisation of the potential offered by stable isotope systems requires an adequate understanding of the factors controlling their isotope fractionation. Various processes such as reduction-oxidation, dissolution-precipitation, and biological utilisation, have been documented to be important controlling factors for Fe isotope fractionation. Here we extend this kind of study to Fe(III) hydrolysis in Cl<sup>-</sup> medium at low temperature conditions.

A solution of 1mg/mL Fe(III) in milli-Q water was prepared from ferric chloride, and 9 mL-aliquots of the solution were loaded into 9 microcentrifuge tubes that were tightly stopped. 5 centrifugal tubes were put in water-bath which was preheated to 46°C, and the others in room (20°C). Duration of the experiments was 95 days. Ferric oxyhydroxide precipitation began after about a day for the experiments at 46°C, whereas it only started after about a month for those at room-temperature. After 95 days, the precipitates and residual solution were separated by centrifuging, and the precipitates were washed with Milli-Q water twice. Both supernates and precipitates were purified through anion exchange chromatography, before Fe isotope measurement using a Nu Plasma HR MC-ICPMS at high-resolution mode. The results are expressed in  $\epsilon$  unit which is deviations in parts per 10<sup>4</sup> from the same isotope ratios of the original FeCl<sub>3</sub> used in the experiments. It is observed that the Fe isotope compositions in precipitates are systematically lighter than those of the corresponding supernates, which is consistent with a previous study (Skulan *et al.*, 2002). The differences between precipitates and supernates in  $\epsilon^{57/54}\text{Fe}$  are  $17.0 \pm 0.8$  and  $20.2 \pm 1.8$  for experiments performed at 20°C and 46°C, respectively.

It has been noticed that the measured Fe concentrations in the supernates are three orders of magnitude higher than those predicted from the solubility constant product for experiments performed at room temperature, whereas the measured and predicted Fe concentrations are similar in the residual solutions for those conducted at 46°C. This suggests that significant amount of ferric oxyhydroxide colloid has not flocculated, but remained in those supernates. Assuming isotopic equilibrium has been reached between the solid and liquid phases for experiments conducted at both temperatures, the Fe isotope composition of the ferric oxyhydroxide colloid must be lighter than that of the solution by at least 3  $\epsilon$  units in  $^{57/54}\text{Fe}$  ratio.

### Reference

Skulan J.L., Beard B. L., and Johnson C.M. (2002). *Geochim Cosmochim Acta* **66**, 2995-3015.

## Origin of ore-forming fluids of the Dajiangping pyrite deposit, South China: Evidence from He-Ar isotopes

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The ore genesis model for the Dajiangping ultra-large pyrite deposit in the South China has long been in dispute, and the major debate focuses on whether the pyrite orebodies were formed by a vapour-liquid superimposition event during hydrothermal alteration, or whether formation of ores was the products of hot-water sedimentation. He and Ar isotopes have been widely applied in tracing the origins and water-rock interactions of contemporary crustal fluids. Recently, these isotope systematics have also been successfully applied to the study of the origin of ancient ore-forming fluids and mineralization. In this work, we report He and Ar isotopic data for the Dajiangping ore deposit for the first time, and discuss the origin and evolution of the hydrothermal fluid.

He and Ar isotope were measured in fluid inclusions from six pyrites in the Dajiangping Deposit. These pyrite samples were collected from different ore types or places: orebody III (banded ores), orebody IV (massive ores), CK36 drill core and wall rocks. The results of helium and argon isotope data are shown that the fluid inclusions from pyrite have  $^3\text{He}/^4\text{He}$  ratios of  $0.18\sim 3.55 \times 10^{-6}$  ( $0.13\sim 2.55\text{Ra}$ ). The values of  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios show slight variation between 348~443, which is higher than air-saturated water's  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios of 295.5(ASW). As shown in the plot of  $^3\text{He}/^4\text{He}$  vs.  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios, the data fall among three sources district, which indicates that the hydrothermal fluid did not originate from the single source, and instead may be a product of crust-mantle mixture. The six pyrite samples come from two orebody IV, two orebody III, one CK36 drill core (depth 133 m), and one wall-rock in study area. We find that the data of fluid inclusion of two pyrites from orebody IV fall in between mantle-derived fluids and ASW. In contrast, the others lie lower on the graph; the CK-36 and DP-11 even lie between ASW and crust fluids.

These data indicate that mantle-derived fluids contributed to the ore-forming fluids. This study suggests that the hot fluids from the mantle intruded into the places of orebody along the thrust faults, and hydrothermed the orebody. This caused differentiation of the two typies orebody to result in the formation of the banded orebody III and the massive orebody IV.

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