

## Iron isotope fractionation during fluid exsolution and evolution

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It is an important issue whether Fe isotopes fractionate during the process of the fluid exsolution from magma and fluid evolution, as this kind of information is crucial in tracing the metal source and mineralization processes using Fe isotopes, and in understanding the evolution of Fe systematics during magmatic and ore-forming processes. Here we examine this issue by systematic investigation of Fe isotope distribution in minerals separates and bulk samples from Xinqiao skarn deposit in Anhui province, China.

Fe isotope compositions of mineral separates of magnetite, pyrite and chalcopyrite, as well as bulk samples of quartz-monzodiorite stock and skarn, were measured using a Nu Plasma HR MC-ICP-MS at high-resolution mode after purification using anion exchange chromatography. The results are expressed as deviations in permil from the same isotope ratios of the reference material IRMM-14.

The skarn is the metasomatic product of magmatic fluid with carbonate country rock, and magnetite is among the earliest iron minerals precipitated from the ore-forming fluid. In this study, the  $\delta^{57}\text{Fe}$  values of endoskarn and magnetite are *ca.* 1.2‰ and *ca.* 0.3‰ lower respectively, relative to the quartz-monzodiorite stock. It has been documented both theoretically and experimentally that significant mass fractionation exists between Fe(II) and Fe(III) species, and Fe(III) enriches heavy isotopes of iron. Therefore, Fe isotope composition of the ore-forming fluid exsolved from the magma must be even lighter than that of the diorite stock. The possibility that light Fe isotope composition of the ore-forming fluid was resulted from mixing with country-rock can be ruled out because the carbonate country-rocks have Fe isotope compositions similar to those of the stock. Spatial and temporal zoning in  $\delta^{57}\text{Fe}$  values is observed in Fe-sulfides, showing that early formed sulfides close to the stock are enriched in  $^{54}\text{Fe}$  compared to the late formed sulfides away from the stock. The most plausible explanation for the observed zoning is that Fe isotopes fractionate between Fe-sulfides and fluid during fluid evolution, and Fe-sulfides preferentially precipitate light isotopes. Thus the Fe isotope composition of residual fluid is becoming heavier with the progress of sulfide precipitation.

The recognition that significant Fe isotope fractionation occurs during fluid exsolution and evolution provides important new insights into Fe isotope behaviour during magmatic evolution and deposit genesis.

## Trace elements and isotope dating from Devonian-Carboniferous boundary in China and its pale environment significance

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This paper makes an analysis of trace elements contained in 16 fossil samples and Rb-Sr dating from Devonian-Carboniferous Boundary at the Nanbiancun section [1] in Guilin, China.

The purposes are to research the pale environment significance and to quantitatively determine the paleoredox environment using the Ce anomaly (-0.49 to -1.7). The clay minerals may be fit in with the Rb-Sr isotopic determination of the boundary age. This is an important support to the conclusion that the section belongs to the Boundary strata and the clay mineral isochron age ( $361.0 \pm 4.1\text{Ma}$ ) is reliable. Our studies showed that the clay is rich in 1Md illite, which is neither of detrital nor of diagenetic origin. This means that the homogenization time of Rb-Sr system can be assumed to be at or close to the sedimentary epoch, and the clay can be reasonably considered as representing the age of the Devonian-Carboniferous Boundary at Nanbiancun, Guilin. The range of 1000 Sr/Ca are 0.5 to 1.2 indicating a lower neritic to shallow bathyal environment.

This study also demonstrates that the reliable age ( $361.0 \pm 4.1\text{Ma}$ ) can be often obtained by using the clay mineral method. Sr isotopic initial ratio is  $0.7079 \pm 0.0002$ . The pale environment significance is determined by the paleoredox environment using the Ce anomaly indicating an oxidized environment of carbonate sedimentation.

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[1] Yu, C.M. (ed) (1988) Science Press, Beijing, China.