

Phosphate-Control of the Yttrium and Rare Earth Element Distribution in Precambrian Banded Iron-Formations: Evidence from a LAM-ICP-MS Study

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The rare earth element (REE) and the Nd isotopic composition of Precambrian Iron-formations (IF) suggest that a significant amount of dissolved REE in Precambrian seawater were supplied by high-temperature hydrothermal fluids from a mantle-source and not by river-water from the continents. Part of the REE in Precambrian IF, therefore, may be derived from seafloor basalts via interaction with high-temperature hydrothermal fluids. This is widely accepted as evidence for a predominantly high-temperature hydrothermal source of IF-bound Fe, too. As a removal mechanism for IF-bound REE from Precambrian seawater it is generally assumed that scavenging by Fe oxyhydroxides was the dominant process. However, the exchange equilibrium between dissolved and sorbed REE is attained within minutes, and lab-studies and studies of natural systems have shown that scavenging produces major fraction within the REE series and between Y and Ho. Hence, the REE pattern and the Y/Ho ratio of a marine Fe oxyhydroxide precipitate (now oxide-facies IF) should differ from those of ambient seawater. If, however, the REE patterns and Y/Ho ratios of IF indeed truly reflect those of contemporaneous seawater, Y and REE scavenging from seawater by Fe oxyhydroxides was either quantitative, or the Y and REE distribution in IF is controlled by other mineral phases.

To learn more about the small-scale inter-elemental associations and the small-scale variation of REE patterns in Precambrian IF we started a LAM-ICP-MS study. Analyses were performed using a standard UV Microprobe laser ablation system, operating at 266nm wave length, which is coupled to a PQX-S ICP-mass spectrometer. We analyzed samples from the 2.5 Ga old, very-low-grade metamorphic, mixed oxide/carbonate-facies, and microbanded Kuruman IF (Transvaal Supergroup, South Africa). Sections of approximately 1cm width, 3cm length and 0.5cm thickness were cut from drill cores and Si, Mg, P, Ca, Fe, Rb, Y, La and Ce were determined along single point ablation profiles perpendicular to bedding. For each individual point 20 replicates of 10s acquisi-

tion time were used to establish a depth profile within one layer. Even at the microscale BIF samples are structurally and compositionally very heterogeneous and hence, no internal standardization could be applied and only intensity ratios can be used for further interpretation. In addition, we performed single point analysis with 60s acquisition time in different types of bands to determine Si, Ca, Fe, P, Y, and the REE. From these analyses REE distribution patterns could be established using relative response values obtained from replicate analyses of the NIST 610 synthetic glass standard.

In none of the analysed subsections exists a significant correlation of Fe with either Ca, P, Y or REE (represented by La and Ce). For the REE, this is in marked contrast to the commonly assumed association of the REE with Fe oxides. The lack of significant correlation between Fe and P further indicates that P is not associated with Fe oxides, suggesting that P occurs as independent phosphate phase. Moreover, there is a positive correlation of Ca and P in one sub-set of the samples, whereas the other shows no such correlation, suggesting that Ca is distributed between Ca-phosphates (apatite) and another phase (possibly carbonate). We further found Y, La and Ce to be (strongly) positively correlated with P, suggesting that Y and REE are not associated with Fe oxides but with Ca-phosphates. This association of Y and REE with phosphate may explain, why the Y-REE signature of many Precambrian IF is very similar to that of seawater. Instead of sorption of dissolved Y and REE on Fe oxyhydroxides (which is accompanied by major fractionation, due to variation between stabilities of solution and surface complexes of Y and the REE), dissolved Y and REE are incorporated in the Ca position of the apatite's crystal lattice. This process is controlled by the charge and radius of the cations relative to those of Ca, and hence, does not produce fractionation between isovalent cations of very similar radius, such as Y and Ho. However, this phosphate-control of the Y and REE distribution may cast doubt on the generally assumed common origin of Fe and REE in Precambrian IF.