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Link between Europium anomaly and isotopic composition of igneous and sedimentary rocks

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Europium (Eu) is a redox-sensitive Rare Earth Element (REE) that switches its valence state from 3^+ to 2^+ under specific temperature, pH and pressure conditions. Previous studies [1] have shown that the change of valence is unlikely to occur at standard conditions (25°C, 1 bar). In contrast, Eu^{3+} is readily reduced to Eu^{2+} at high temperatures under mildly acidic conditions. This redox behavior is believed to be responsible for the fractionation of Eu from other REEs, resulting in strong positive Eu anomalies in REE patterns. This is for example the case of plagioclase-rich lithologies (e.g. basalt), hydrothermal fluids and associated deposits. In this study, we investigated the relationship between Eu anomaly and Eu isotopic composition in geological reference materials and few Archean sedimentary, chemical rocks.

We developed a three-stage column chemistry based on ion chromatography techniques to separate Eu from sample matrix. Europium isotopic composition, expressed as ε_{Eu}, was measured by MC-ICP-MS relative to the NIST 3117a standard. The estimated repeatability of our procedure is at 0.5 ε units, based on repeated analyses of NIST standards processed through the whole chemical procedure. Common igneous reference materials (e.g., BHVO-2, AGV-1, BCR-2, BIR 1a, G-2, and RG-M) produced ε_{Eu} values indistinguishable from the NIST standard ($\varepsilon Eu = 0 \pm 0.5$) despite their large range of Eu anomalies ($0.5 < Eu/Eu^*_{CN} < 1.5$) and SiO_2 contents. Similarly, terrigenous, sedimentary reference materials, such as JLk-1 and JSd-2, show no significant Eu isotopic fractionation. Small Eu isotopic fractionation was suggested for differentiated igneous rocks by Lee and Tanaka (2021) [2], but we were not able to confirm this trend. However, we identified resolvable fractionations, up to 2.9 epsilon units, in Fe-rich sedimentary standards such as FeR-1, FeR-2, FeR-3, and IF-G, having all positive Eu anomalies ($Eu/Eu^*_{PAAS} > 3$). FeR-2, FeR-3, and IF-G are Archean banded iron formations for which Eu anomalies have previously been interpreted to reflect high-temperature, hydrothermal activity. Our results suggest that Eu isotopic composition, as well as Eu anomaly, trace high-temperature hydrothermal processes.

[1] Bau (1991), Chemical Geology 93, 219-230

[2] Lee and Tanaka, Geochemical Journal 55, 9-17