

Cerium stable isotope ratio in ferromanganese deposits and its potential as a paleoredox proxy

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Cerium (Ce) anomaly observed in rare earth element (REE) patterns has been used to estimate the redox state of paleo-marine environments. Cerium is unique because it forms tetravalent cations under oxic condition, in contrast to other REEs that occur in a trivalent state. This characteristic leads to anomalously high or low Ce concentrations relative to neighboring REEs. However, the use of Ce anomaly as a paleo-redox proxy is not well calibrated. This study shows that coupling of the Ce anomaly and Ce stable isotope ratio ($\delta^{142}\text{Ce}$) is a more quantitative redox proxy to distinguish suboxic and oxic redox conditions. Our results revealed a progressive enrichment in heavy Ce isotopes in consecutive formations of iron (Fe) and manganese (Mn) precipitate from hot spring water without any associated change in REE patterns. The $\delta^{142}\text{Ce}$ values of Mn precipitates were approximately 0.35‰ heavier than those of the Fe precipitates, which was consistent with experiment-based predictions. The $\delta^{142}\text{Ce}$ values of marine ferromanganese deposits with three different formation processes were hydrogenetic (+0.25‰) > diagenetic (+0.10‰) \geq hydrothermal (+0.05‰), which also reflects redox conditions of their formation environment. These observations suggest that the Ce stable isotope ratio yields more quantitative information regarding redox state than REE patterns alone. We thus suggest that this novel proxy can be successfully utilized to reconstruct marine redox states, particularly from slightly oxic to highly oxic conditions such as the Great Oxidation Event (GOE).

Reference

R. Nakada, Y. Takahashi, and M. Tanimizu (2016)
Geochim. Cosmochim. Acta, vol. 181, p. 89–100.