

New techniques for separation and analysis of Lu-Hf, Sm-Nd and the REE by MC-ICP-MS

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We have developed new techniques for rapid and reproducible analysis of the Lu-Hf and Sm-Nd isotopic systems, as well as ID analysis of the REE by MC-ICPMS. Samples for Lu-Hf and Sm-Nd isotopic analysis are fused with LiBO₄ and the melt is dissolved in weak HNO₃, spiked with ¹⁷⁶Lu-¹⁸⁰Hf and/or ¹⁴⁹Sm-¹⁵⁰Nd tracers. After a pre-concentration step for HFSE and REE by Fe-hydroxide coprecipitation, Lu and HFSE+REE cuts are recovered from a cation exchange column with 4 and 6 M HCl. Hf is separated from the HFSE+REE cut using TEVA-SPEC resin in high molarity HCL; the LREE may be saved from this step enabling Sm-Nd isotopic determinations on the same sample digestion. Hf yields are > 90% while total procedural blanks are < 100 pg (Hf) and < 10 pg (Lu), even for large (0.3 g) low-Hf samples with variable matrix compositions like meteorites, apatites and garnets. Multiple analyses of a range of Standard Reference Materials yields a reproducibility of < 0.2% on Lu/Hf ratios. Even difficult to digest samples only take two days to digest and separate Lu-Hf and Sm-Nd for analysis.

Samples for REE ID analysis are digested by standard acid digestion techniques. M-HREE and LREE are collected from a cation exchange column, which provides a M-HREE cut with sufficient separation from the LREE to render oxide interferences trivial, and a Ba-free LREE cut. Heavy, middle and light REE concentrations are determined by three 1-2 min analyses. Replicate digestions of international standards demonstrates that concentrations reproduce to < 1%, and inter-REE ratios reproduce to ≤ 0.2% (2 sd). Eu and Ce anomalies reproduce to < 0.15%. Mono-isotopic Pr can also be measured during the LREE isotope dilution run, by reference to Pr/Ce and Pr/Nd ratios measured in a REE standard solution. Pr concentrations determined in this way reproduce to < 1%, and Ce anomalies calculated using La and Pr also reproduce to < 0.15% (2 sd). The precise Ce (and Eu) anomaly measurements should allow greater use of these features in studying crust-mantle recycling, or redox-induced affects on the REE during recycling and dehydration of oceanic lithosphere, partial melting, metamorphism, alteration and/or sedimentation processes. This technique for measurement of the REE is superior in terms of the analytical reproducibility or rapidity of analysis compared with quadrupole ICP-MS or TIMS ID techniques and consumes sub-ng amounts of the REE. We will report on a high precision REE study of oceanic basalts and chondrites, particularly with respect to evaluating Ce anomaly variations in these materials.

Mg isotopic compositions of W-L and accretionary rims of CAIs

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Introduction

It is known that common type CAIs such as Types A, B and C, which are frequently found in CV chondrites, have layered rim structures which are called as Wark-Lovering rims (W-L rims). W-L rims consist of three layers: spinel (and minor perovskite) layer, melilite (or its alteration products, e.g. anorthite, nepheline) layer and diopsidic pyroxene layer, from interior to exterior. It is also known that CAIs are sometimes surrounded by fine-grained mineral layers which are called as accretionary rims. Although ¹⁶O-rich signatures observed in W-L rims and accretionary rims suggest that the origin of these layers relates to the CAI formation event, it is not known how these rim structure formed. Here we present preliminary results of Mg isotopic measurements of interior, W-L rims and olivine in accretionary rims of CAIs.

Results and Discussions

Mg isotopic measurements were performed for two type A CAIs and two type B1 CAIs with an ion microprobe. Matrix effects were determined and corrected using terrestrial minerals. All CAIs have positively fractionated Mg isotopes in their interior with a fractionation factor, F_{Mg} , of +2 to +10‰/amu relative to PO chondrules (assuming $F_{Mg} \sim 0‰/amu$). F_{Mg} of spinel in the W-L rims is similar to that of spinel in the interior of CAIs. F_{Mg} of diopsidic pyroxene in the W-L rims and that of olivine in the accretionary rims, in contrast, are smaller than that in the interior of CAIs (-3 to +2‰/amu).

It is suggested that spinel in the W-L rims is closely related to (spinel in) the interior of CAIs. It is also suggested that diopsidic pyroxene in the W-L rims and olivine in the accretionary rims are different from the interior and spinel in the W-L rims of CAIs in view of Mg isotopes.

Recently, a flush heating process was proposed for the formation of W-L rims. It seems, however, difficult to explain the present results. We consider that spinel layer and pyroxene layer of W-L rims formed by separate processes and that the latter possibly formed by a condensation process.

References

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