

## Chondrite Barium, Neodymium and Samarium isotopic heterogeneity and early Earth differentiation

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Understanding the early earth differentiation requires using a cosmochemical reference that represents the bulk composition of the planet. The difference of ~20 ppm measured between chondritic and terrestrial <sup>142</sup>Nd/<sup>144</sup>Nd have been interpreted to reflect an early silicate differentiation of the Earth [1], <sup>142</sup>Nd being formed through time by the radiogenic decay of <sup>146</sup>Sm (half-life = 103 Myr). A critical requirement in this application is demonstration that the small isotopic variations do not simply reflect isotopic heterogeneity in the Solar nebula caused by imperfect mixing of the various stellar contributions [2].

New determinations of Ba, Nd, and Sm isotopic composition in 12 chondrites from different groups show that carbonaceous chondrites contain well-resolved s- and p-process deficiencies in these elements relative to ordinary and enstatite chondrites. Using <sup>148</sup>Nd/<sup>144</sup>Nd to correct for the observed s-process deficiency produces a chondrite <sup>146</sup>Sm-<sup>142</sup>Nd isochron that is consistent with previous estimates of the initial Solar System abundance of <sup>146</sup>Sm and a <sup>142</sup>Nd/<sup>144</sup>Nd at average chondrite Sm/Nd ratio that is 21 ± 3 ppm lower than measured in terrestrial rocks [2, 3]. This result strengthens the conclusion that the deficiency in <sup>142</sup>Nd in chondrites compared to terrestrial rocks reflects <sup>146</sup>Sm decay.

Despite showing large variation in Lu/Hf, both refractory and lithophile elements like the REE, chondrites from different groups show little variation in their Sm/Nd ratios. No chondrites measured so far have <sup>147</sup>Sm/<sup>144</sup>Nd high enough to explain the terrestrial <sup>142</sup>Nd/<sup>144</sup>Nd. The p-process deficits in <sup>144</sup>Sm measured in carbonaceous chondrites suggest that ordinary and enstatite chondrites are better analogs for the bulk composition of the earth. Only superchondritic <sup>142</sup>Nd/<sup>144</sup>Nd have been measured in terrestrial rocks. These results suggest that a major volume of Earth's mantle was depleted in incompatible elements as a result of magma ocean crystallization. We are pursuing evidence for the presence of the complementary enriched reservoir, which should be preserved in the deep mantle despite 4.5 Gyr of mantle convection.

### References

- [1] Ranen and Jacobsen, *Science* **314**, 809;
- [2] Boyet and Carlson 2005, *Science* **309**, 576;
- [3] Andreasen and Sharma, *Science* **314**, 806.

## Ensuring accuracy in high-precision isotope ratio measurements

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Recent improvements in isotope ratio measurement precision are most clearly associated with physical improvements in the instruments used to make these measurements. Factors such as faraday cup efficiency, detector linearity and dynamic range, and consistent ion focussing clearly were critical in pushing precisions below the 10 ppm level. A number of other factors enter into the precision, and particularly the accuracy of isotope ratio measurements at this level. Common to both TIMS and ICP-MS are the question of the correct form of the instrumental mass fractionation correction, and the difficulty of detecting, and correcting for, isobaric interferences that may be a million times smaller than the signal analysed. ICP sources and the desire to measure stable isotope fractionation add another suite of issues that include: a richer and more complex atomic and molecular interference spectrum; the need to correct for sample mass fractionation that may occur during sample volatilization (in laser ablation), chemical separation, introduction into the plasma (particularly when using desolvating nebulizers), evaporation and ionization in the plasma, ion-electron separation, and ion extraction and focussing. Simple mass-only dependency of fractionation in the ICP was revealed as a myth as precisions moved from the hundreds to tens of ppm range. Many of these issues add to our dependency on high quality standards to ensure interlaboratory comparison. For TIMS Nd, for example, all available standards have more Ce and Sm than rock samples separated using modern procedures. For ICP-MS, standard comparison often cannot be done with relatively easily prepared single-element solutions, but requires standards with matrices similar to the samples being analysed to show that chemical separation and sample introduction effect standard and sample in similar ways. With care, these issues can be dealt with well enough to obtain isotope ratio precisions within a factor of 2 to 4 of counting statistics. Therefore, future precision improvements are likely to come from instruments that produce nanoamp beams from micrograms of sample instead of picoamps from nanograms, and have faraday detectors that can maintain perfect collection efficiency at this increased level of abuse. Improving precision of small sample analysis likely will depend primarily on improved sample utilization (delivery, ionization and transport) efficiency and on the development of electron multipliers that provide better linearity, dynamic range and longevity.