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European Association for Geochemistry - Houtermans Medal Lecture
An introduction to the isotope geochemistry of magnesium

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Differences in the relative abundances of Mg three stable isotopes, ^{24}Mg (78.99%), ^{25}Mg (10.00%), and ^{26}Mg (11.01%), could be expected because of the large relative mass differences between ^{26}Mg and ^{24}Mg. However, Mg-bonds are dominantly ionic and while kinetic processes affect all elements, thermodynamic isotopic equilibrium has only been demonstrated for elements involved in strong chemical bonds. In addition, reliable measurements of ^{25}Mg/^{24}Mg and ^{26}Mg/^{24}Mg in natural systems have been limited historically by the 1‰/amu reproducibility imparted by instrumental mass fractionation effects. As a result, with a few exceptions, studies of Mg isotope ratios focused on detection of non-mass dependent Mg isotopic effects rather than on investigations of mass-dependent fractionation. The principle outcome of this focus was the discovery of radiogenic ^{26}Mg in primitive meteorites 30 years ago.

Technical breakthrough

With the advent of MC-ICPMS it is now possible to measure ^{25}Mg/^{24}Mg and ^{26}Mg/^{24}Mg in solution with a reproducibility of 0.06‰/amu [1]. These new analytical capabilities allow mass-dependent fractionations of the isotopes of Mg to be used as tracers in natural systems.

Since the only Mg reference material available appears to be heterogeneous in its isotopic composition, a new primary standard has been developed [2]. It consists of pure Mg metal dissolved in nitric acid. This material, referred to as DSM3, is a suitable reference material because it is already in solution and therefore immune to heterogeneity. Mg isotopic composition are expressed as a permil deviation from the isotopic composition of the standard: δ^{x}Mg $=\{(^{x}Mg/^{24}Mg)_{Sample}/(^{x}Mg/^{24}Mg)_{DSM3} - 1\} \times 1000$, (where X = 25 or 26).

Mg isotope reservoirs

Whole rock samples of CI meteorite and pyroxene from mantle nodules are indistinguishable from the DSM3 and suggest that δ^{26}Mg = 0.0 ‰ is a reasonable estimate of the chondritic reservoir for Mg [2-4]. The olivine is enriched in light isotope by 0.9‰ with respect to the pyroxene. However, there is concern that these olivine may have been altered and claims for mineral-specific heterogeneity in mantle δ^{26}Mg on the order of 0.8 ‰ would be premature. Loess and the continental basalts suggest that evolved crustal materials may be on average approximately 0.4 to 0.6 ‰ lower in δ^{26}Mg than the primitive CI/mantle reservoir. The magnesium isotope composition of seawater to be constant, with a δ^{26}Mg = -0.82 ‰ [5].

Evidence for equilibrium isotopic fractionation

Differences between δ^{26}Mg in the water dripping from stalactites and that of the modern speleothem show that the low Mg-calcite is enriched in light isotopes by 2.7‰ and the dependence on temperature has been found to be less than 0.04‰/ºC [6]. Given that 1) O isotopic equilibrium fractionation between the water and the carbonate is achieved in one case, 2) kinetics of speleothem formation are drastically different between the studied karsts; a kinetic-related isotopic fractionation would have induced a broader range of the observed isotopic fractionation. Further evidence that Mg-isotopes have reached equilibrium during formation of the speleothem is given by a value of the slope in the three-isotope plot of 0.5190 +/- 0.0029. This value is equals, within error, to the theoretical expectation [4].

Conclusion

These results have two implications. 1) during the weathering, Mg-isotopes will not necessarily only witness biological activity. 2) Mg-isotopic variations are induced by thermodynamic equilibrium reactions characteristic of common geological processes. Associated to more conventional isotopic systems (i.e. O and H), Mg isotopes appear to have a more widespread application than previously thought. Our understanding of processes involving isotopic fractionations is, however, crucial for a clear interpretation of new isotopic tracers.

References

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