Ca isotope fractionation during Ca-carbonate precipitation: There's more to it than temperature

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The use of the Ca isotope composition of calcite produced by foraminifera as a "paleo-thermometer" has been the subject of numerous recent studies. δ^{44}Ca (the per mil difference of the ^{44}Ca/^{40}Ca ratio of a sample from that of seawater) of Ca in natural and experimentally-cultured foraminiferal calcite is 0 to 2 per mil more negative than that of coexisting aqueous Ca, and the extent of fractionation has been attributed to a dependence on both the temperature of calcite formation and the particular species involved. The fact that Ca in the calcte is isotopically lighter than coexisting aqueous Ca provides one of the more intriguing results of this work, and suggests that the isotopic lightness of the calcte may be due to "kinetic isotope effects" associated with biological processing of Ca. However, there are important physical controls such as carbonate precipitation rate that can affect isotopic fractionation, and it is essential to understand their influence before any paleothermometry application can be considered robust and extended to other materials such as aragonite of corals.

For the present study, we conducted a series of abiotic experiments in which calcite and aragonite were synthesized at 10°C, 25°C and 40°C, and at various precipitation rates. At each temperature, the carbonate precipitation rate was varied by controlling the rate of decarbonation of the reactor, either by adjusting the flow of N_2-gas bubbled through the reactor or by allowing the reactor to decarbonate without inducement. δ^{44}Ca was measured on carbonate and aqueous products using thermal ionization mass spectrometry with a ^{42}Ca-^{48}Ca double spike amendment to correct for fractionation during the entire analytical procedure. We found that at rapid precipitation rates, $\alpha_{\text{carbonate-aqueous Ca}}$ increased significantly with increasing temperature in both the calcite and aragonite systems. However, at slow precipitation rates $\alpha_{\text{carbonate-aqueous Ca}}$ was essentially constant in both systems over the temperature range of the experiments and similar to that of the experiments at 10°C and rapid precipitation rate. Increasing Ca isotope fractionation with decreasing carbonate precipitation rate at 40°C suggests that the isotopic lightness of Ca in carbonate is not due to kinetic isotope effects, but rather to equilibrium isotope effects and the weaker bonding of Ca in the carbonate structure relative to that in aqueous complexes. Further, our results suggest that the Ca isotope "paleo-thermometer" may not be as robust as previously assumed, indicating the need for further exploration of processes that fractionate Ca isotopes.

Chondritic building blocks of Vesta

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Introduction

All planetary bodies in our solar system are believed to have condensed out of material from the solar nebula. Chondritic meteorites represent samples of this "primitive" material. However, none of the planets appears to be an "exact" isotopic and compositional match for any single chondrite type. One planetary body for which we have detailed compositional information is asteroid 4 Vesta, the probable parent body of the howardite, eucrite, and diogenite (HED) meteorites. We evaluated ~225 million combinations of the 13 chondritic groups in an attempt to determine the best oxygen isotopic and compositional matches to Vesta.

Results

A computer program was developed that inputs average oxygen isotopic values as well as average compositional data for each chondritic group. Aggregate isotopic and compositional values for every possible combination of these meteorites at mass increments of 5% were computed. Elements and compounds were combined linearly except for the oxygen isotopic values, which were weighted by the oxygen content of each meteorite. Redox reactions were used to determine the FeO content of each matching combination.

To determine possible matches, we used isotopic and compositional constraints derived from HED meteorites. We assumed a Δ^{17}O (‰) = -0.26 ± 0.08, a ∂^{17}O (‰) = 1.52 ± 0.26, and a ∂^{18}O (‰) = 3.41 ± 0.50. The bulk FeO content of Vesta was assumed to be 15.6 ± 1.6 wt.%.

There were ~560,000 matching combinations (0.25% of the total). The ordinary chondrites might comprise up to 75-80% of a mixture, but carbonaceous chondritic material is also necessary to match Vesta's oxygen isotopic composition and FeO content. This result is similar to the conclusions of Boesenberg and Delaney (1997).

CM2 and CR2 fragments are found in howardites and have been proposed as building blocks of Vesta. Among our matching combinations, CR2 material can comprise up to 50% of a mixture, but CM2 material can only represent up to 10%.

References

Boesenberg J. S. and Delaney J. S., (1997), *Geochim. Cosmochim. Acta* **61**, 3205-3225.