



Kinetic and equilibrium Ba isotope fractionation during carbonate precipitation

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Variations in stable isotope ratios recorded in carbonates are widely used to reconstruct the physicochemical conditions, e.g., pH, temperature and redox conditions, prevailing at the time of carbonate mineral formation. Knowledge of isotope fractionation factors during mineral precipitation under varying environmental conditions is irremissible for the interpretation of isotope variations in natural sedimentary archives. However, experimentally derived fractionation factors, of for instance Ca isotopes, are often ambiguous and incommensurable due to differences in experimental parameters.

Here, Ba isotope fractionation during carbonate mineral formation was investigated [1]. Time-resolved experiments of witherite (BaCO_3) precipitation revealed an initial kinetic isotope effect with increasing $\Delta^{137/134}\text{Ba}$ values of the ambient solution, following Rayleigh fractionation ($\alpha_{\text{witherite-fluid}} = 0.99993 \pm 0.00004$). After precipitation, the witherite crystals remained in contact with the ambient solution for about nine days. During this time, chemical steady state was achieved between solution and witherite; however, the $\Delta^{137/134}\text{Ba}$ values of the solution decreased. At isotopic equilibrium, the ambient solution and the witherite crystals exhibited identical $\delta^{137/134}\text{Ba}$ values, within the analytical uncertainty of $\pm 0.04 \text{‰}$. This observation is interpreted as the result of continuous exchange of Ba^{2+} ions between witherite and solution after initial preferential uptake of the lighter Ba isotopes in the precipitating carbonates. Mass balance calculations indicate that the ion exchange affects several subsurface layers of the crystals. In summary, Ba isotope exchange between carbonate and ambient solution occurs at chemical equilibrium, and pristine isotopic signatures in carbonates may thus be reset at low temperatures.

[1] Mavromatis et al. (2016) *Geochim. Cosmochim. Acta* 190, 72-84.