Experimental Study of Sr, Mg, and Ba Partitioning Into Calcite at Various Linear Growth Rates Using Elemental and Isotopic Spikes: Preliminary Results.

R.I. GABITOV, J.F. ADKINS, AND J.M. EILER

The ratios of Mg/Ca and Sr/Ca in calcium carbonates are widely used as paleothermometers. However, inconsistencies in the relationship between temperature and composition amongst inorganic and biogenic calcites suggest the influence of factors other than temperature [1,2], including precipitation rate [3,4]. We examine the influence of growth rate on Mg, Sr, and Ba partition coefficients between calcite and aqueous fluid \( K'_d = \frac{X_i^{\text{Calcite}} X_{\text{Ca}}^{\text{Fluid}}}{X_i^{\text{Calcite}} X_{\text{Ca}}^{\text{Fluid}}} \), where \( i \) is the cation of interest and \( X \) is the mole fraction). Previous experimental studies of growth-rate-dependent partitioning were based on bulk analysis of carbonate precipitates [3,4]; here we develop an alternative approach based on in situ measurements of single crystals having known linear growth rates.

Experiments were performed by continuously adding two titrates (Na\(_2\)CO\(_3\) and CaCl\(_2\)) into growth solution of NaCl doped with trace elements. Compressed air was bubbled through the growth solution. The values of pH and total dissolved carbon were monitored over the course of each experiment. Linear growth rates of calcite crystals are determined by adding of elemental and isotopic spikes into the growth medium (episodically for elemental spikes; continuously for isotopic spikes). Harvested crystals were randomly mounted into high vacuum epoxy and examined with NanoSIMS and SEM techniques.

Our NanoSIMS measurements of product calcite crystals document approximately concentric growth, the rate of which is marked by the sequential appearance of the various elemental and isotopic spikes we added to the parental fluid during growth. For example, ratios of \(^{55}\text{Mn}/^{42}\text{Ca}\) in carbonate are \( \leq 10^{-5} \) in crystal cores and sharply increase up to \( 1.6 \times 10^{-3} \) in crystal rims, in response to our addition of Mn to the parental liquid at a known time. Similarly, the \(^{26}\text{Mg}/^{24}\text{Mg}\) ratio is close to natural abundances in crystal cores and monotonically increases toward the crystal edges, reflecting monotonic addition of \(^{26}\text{Mg}\) spike throughout the experiment. Such data, combined with known timing of elemental spike additions and rates of increase of the \(^{26}\text{Mg}/^{24}\text{Mg}\) ratio of the solution, permitted us to quantitatively reconstruct the growth histories of individual calcite crystals. Calcite growth rates were calculated as the ratio of the distance between two adjacent analytical spots and the corresponding time interval required to explain their difference in composition. This is straightforward for the portions of the experiments when \(^{26}\text{Mg}/^{24}\text{Mg}\) changed.
monotonically at a known rate, but generally provides only limits to the growth rate during the period when elemental spikes were added episodically. The linear growth rates estimated in this way varied from 0.6 to 6 microns per hour, with uncertainties as good as 6%, relative. The lower edge of our growth rate interval is similar to those of benthonic foraminifera [5], suggesting that partitioning data based on our experiments will constrain growth-rate effects relevant to common paleothermometry applications. Note that the growth rates we derive could be under-estimates because analyzed sections of the crystals do no necessarily expose the center of calcite crystallization. We anticipate determining Sr/Ca, Mg/Ca, and Ba/Ca ratios in the fluid, after which we shall report the partition coefficients for Sr, Mg, and Ba as function of growth rate of the calcite crystals.

References