

Specific Effects of Background Ions on Magnesium Incorporation into Calcite

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INTRODUCTION.

Trace metal incorporation during mineral growth is a critical factor controlling the reactivity and cycling of metals in biogeochemical systems, and therefore, it is of paramount importance for understanding and predicting numerous natural processes occurring in the Earth. In particular, trace element signatures in biogenic marine carbonates are widely used as proxies for reconstructing past ocean chemistry and paleoclimate. Magnesium is present in oceans with a nearly constant ratio to calcium of ca. 5. Variation in Mg/Ca in marine cements and calcified skeletal structures can be related to changes in other environmental parameters that control magnesium incorporation into calcite. This is the background, for example, for the use of Mg/Ca ratio of marine carbonates as a proxy for reconstructing sea surface temperature. However, several studies have shown that the Mg/Ca ratio in calcite is controlled not only by temperature, but also by other parameters, such as pH, CO_3^{2-} or salinity (Dissard et al., 2010 and refs. therein). The effect of all these parameters should be quantified separately before reliable information regarding sea surface temperature can be extracted from the Mg/Ca ratios in biogenic marine carbonates. For example, the impact of salinity on Mg incorporation into calcite is still poorly understood (Dissard et al., 2010). The effect of salinity is generally considered to arise from changes in the ionic strength of the precipitating fluids. Here we show that the specific hydration characteristics of the background electrolyte used to create the ionic strength have also an impact in incorporation of magnesium.

METHODOLOGY.

Macroscopic growth rates were

determined on calcite single crystals of known mass, each placed at the bottom of a stirred flow-through reactor. Freshly cleavage calcite crystals (ca. 4x3x1 mm size) were weighted on a micro-balance, with a resolution of 1 μg , and transferred into the flow-through reactors. Teflon® reactors with an inner volume of 63 cm^3 were used. A detailed description of the experimental set-up can be found in Nehrke et al (2006). Flow was adjusted to 120 mL h^{-1} , which gives a residence time of ca. 0.5 h. All experiments were performed at a constant laboratory temperature of 22 ± 0.2 °C. In order to maximize the growth rate, the solution stoichiometry, defined as the ratio of the activities of lattice ions in solution ($a_{\text{Ca}}/a_{\text{CO}_3}$), was made equal to 1 by adjusting the amount of Na_2CO_3 and $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ at a fixed pH of 10. The supersaturation, Ω , was calculated as $\Omega = \text{IAP}/K_{\text{sp}}$ where IAP is the ion activity product and K_{sp} the solubility product of calcite ($10^{-8.48}$). The solution supersaturation was set constant at 19. Four different experiments at two different ionic strengths (IS) were performed: two using NaCl as background electrolyte (IS = 0.006 and 0.1) and two using Na_2SO_4 as background electrolyte (IS = 0.006 and 0.1). Mg concentration in all experiments was 0.4 mM. At the end of each experiment, crystals were weighed to determine the mass of calcite grown during each experiment. The Mg contents of the overgrowths were determined by electron microprobe analysis (EMP).

RESULTS AND DISCUSSION.

Oscillatory compositional zoning.

Figure 1 shows a typical Mg distribution map obtained by EMP analysis. Periodically distributed bands with different Mg content were observed in the calcite overgrowth. Oscillatory

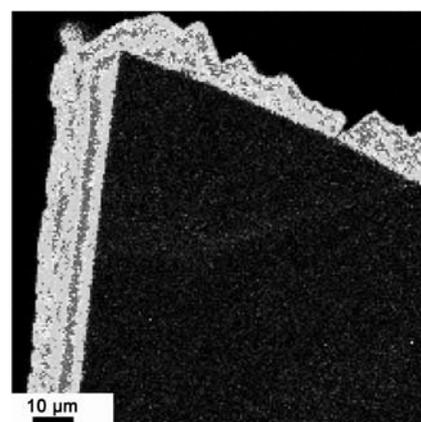


fig 1. Mg-distribution map of transversal section of the calcite crystal after the growth experiments obtained by EMP. Differences in tone are due to differences in Mg content. Background Electrolyte: NaCl, Ionic Strength = 0.1.

compositional zoning is a frequent phenomenon observed in crystal growth processes. It has been previously recognized for major elements in $(\text{Mg,Ca})\text{CO}_3$ (Fernández-Díaz et al., 1996) and $(\text{Ba, Sr})\text{SO}_4$ solid solutions (Putnis et al., 1992), as well as for the distribution of trace metals in calcite (Wang and Merino, 1992). This process can be explained by considering that the initial growth of a solid with a calcium-rich composition (i.e. depleted in magnesium) results in an increase in the relative concentration of magnesium in the fluid in contact with the solid, until the threshold supersaturation for the nucleation and growth of a solid with a more magnesium-rich composition is reached. The growth of such a solid depletes the solution in magnesium, resulting in a period of less magnesium-rich growth (Putnis et al., 1992). These changes in solution composition are likely to occur in the boundary layer in contact with the surface, as the bulk solution will be characterized by a constant composition due to continuous high flow rate and the stirring. Nevertheless, in our case the differences in Mg-concentration found among these

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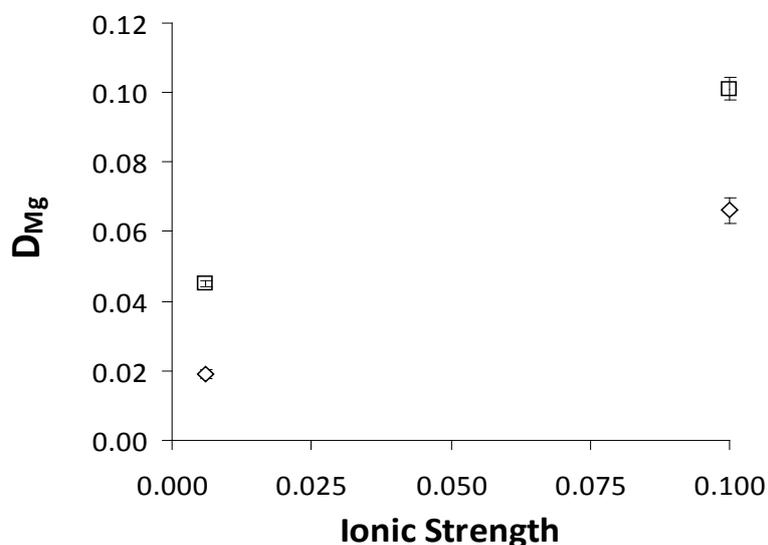


fig 2. Magnesium distribution coefficient in calcite as a function of ionic strength, for crystals grown in (◇) NaCl- and (□) Na_2SO_4 -bearing solutions.

bands where less than 0.4 % weight of MgO. For simplicity, a single (average) value for the rim was used for the calculation of distribution coefficients (see next section).

Mg distribution coefficients.

Table 1 reports calcite growth rates, Mg composition of the overgrowths and calculated magnesium distribution coefficients (D_{Mg}) between the calcite and the solution for our experiments. D_{Mg} can be defined as

$$D_{Mg} = \frac{X_{Mg} / X_{Ca}}{a_{Mg} / a_{Ca}} \quad (1)$$

where X denotes molar concentration in the solid and a denotes activity in solution. D_{Mg} data are plotted as a function of ionic strength for the two different background electrolytes tested in Figure 2. In experiments with the same background electrolyte, D_{Mg} increases with calcite growth rate (which increases with IS). Experimental partition coefficients are known to be strongly growth rate-dependent (see for example Rimstidt et al., 1998, and refs. therein). Trace elements (Tr) such as Sr, Ba and Mg, have $D_{Tr} < 1$, meaning that they are excluded from calcite (in other words, they are preferentially partitioned into the solution). The value of the experimental partition coefficient for these elements increases systematically with increased calcite growth rate. However, no correlation was found in our

experiments between D_{Mg} values and measured growth rates when data from the two background electrolytes are considered. In general, as can be seen in Table 1 and Figure 2, Mg partition coefficients (at a constant IS) are higher in SO_4 -bearing solutions. SO_4^{2-} ions are known to be strongly hydrated in solution. As a consequence, they reduce the mobility of water around them, which results in increasing the frequency of water exchange around Mg^{2+} ions, thus facilitating their incorporation into calcite.

CONCLUSIONS.

Temperature is not the only parameter controlling the extent of Mg incorporation in calcite from solutions with a constant Mg/Ca ratio. Apart from the well-known control exerted by the surface structure at the mineral-solution interface (Paquette and Reeder, 1995), our experiments show clearly that the ionic strength and, remarkably, the specific character of the ions generating it, have also a strong impact on cation uptake. This may influence the

composition of natural calcites. Also, we show that the composition of the fluid in the boundary layer in contact with the mineral surface controls the incorporation of Mg for a constant bulk fluid composition. Depletion and enrichment in Mg in this boundary layer (as a result of the growth of a Mg-rich and Mg-poor composition), result in compositional oscillatory zoning in the overgrowth.

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Background Electrolyte, IS	Growth Rate	Std	Mg in the overgrowth	Std	D_{Mg}	Std
NaCl, 0.006	0.0678	0.0136	0.730	0.104	0.0191	0.0012
NaCl, 0.1	0.3568	0.2489	1.515	0.174	0.0661	0.0036
Na_2SO_4 , 0.006	0.0018	0.0026	1.565	0.064	0.0453	0.0009
Na_2SO_4 , 0.1	0.7942	0.0403	1.207	0.080	0.1012	0.0031

Table 1. Summary of the results of flow-through experiments. The growth rate is given in $\mu\text{mol}/\text{cm}^2\text{-h}$ and the overgrowth content of magnesium is given in MgO % weight. IS stands for ionic strength.