



# Strontium incorporation during calcite growth: Implications for chemical mapping using friction force microscopy



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## ARTICLE INFO

### Article history:

Received 8 October 2014

Received in revised form 7 July 2015

Accepted 8 July 2015

Available online 11 July 2015

Editor: Carla M Koretsky

## ABSTRACT

Sr partitioning on calcite crystals growing from  $\text{Ca}^{2+}$ – $\text{Sr}^{2+}$ – $\text{CO}_3^{2-}$  solutions was studied by means of friction force microscopy (FFM). Experiments were performed with various  $\text{Sr}^{2+}_{(\text{aq})}/\text{Ca}^{2+}_{(\text{aq})}$  concentration ratios and total  $\text{Sr}^{2+}_{(\text{aq})}$  concentration in order to examine conditions under which Sr-calcite growth is self-limiting (e.g., the so-called “template effect”) and also to investigate continuous Sr-calcite growth, where spiral growth predominates and Sr incorporation is sector-dependent. In these latter experiments, the goal was to evaluate the utility of friction force microscopy to discriminate sector zoning. Results from the experiments show that friction increases with the incorporation of Sr into the growing calcite layers. The maximum increase in friction was measured at high  $\text{Sr}^{2+}_{(\text{aq})}/\text{Ca}^{2+}_{(\text{aq})}$ , although a quantitative link between a specific amount of increase in friction to a specific amount of Sr incorporation was not possible to determine due to experimental uncertainties. Nevertheless, it was possible to establish that no change in friction is detectable when Sr incorporation yields a solid composition of  $\text{Sr}_{0.05}\text{Ca}_{0.95}\text{CO}_3$ . Friction was found to increase during growth of several layers in an incremental fashion. The increase can be linked either to an incremental increase in Sr content in the newly formed calcite, controlled by the thermodynamics of the strained layers necessitated by the substitution of larger Sr cations into the calcite, or to the incremental increase in layer thickness which in turn leads to increases in the probe-surface contact area. No difference in friction could be observed between acute and obtuse sectors under any of the experimental conditions, which was primarily due to the limits of the friction measurement sensitivity.

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## 1. Introduction

The interactions between carbonates and metal-bearing solutions have received considerable attention in the literature (Andersson et al., 2014; Bracco et al., 2012; Davis et al., 2004; Kohler et al., 2007; Lorens, 1981; Nielsen et al., 2013; Paquette and Reeder, 1995; Reeder, 1996; Tesoriero and Pankow, 1996), due to the ubiquity of carbonates in the Earth's crust and their ability to interact with various divalent metals with significant environmental and geochemical implications. In particular,  $\text{Sr}^{2+}_{(\text{aq})}$  interactions with calcite have been studied due to calcite's potential use as a proxy for paleoenvironmental reconstructions (Carpenter and Lohmann, 1992; Stoll et al., 2002; Tang et al., 2008; Tang et al., 2012) and biocrystallization (Lea et al., 1999), with studies spanning from bulk experiments (Mucci and Morse, 1983; Pingitore et al., 1992; Tang et al., 2008; Tang et al., 2012), to microscale investigations using single crystals (Gabitov et al., 2014; Nehrke et al., 2007) to detailed nanoscale observations using atomic force microscopy (Astilleros et al., 2003a; Bracco et al., 2012; Wasylenki et al., 2005).

Accordingly, the goals of these studies have been to study the Sr effect on crystal growth rates/mechanism, as well as its partitioning into the newly grown phase.

Atomic force microscopy observations by Astilleros et al. (2003a) showed a variety of phenomena on calcite surfaces exposed to  $\text{Sr}^{2+}_{(\text{aq})}$  solution, depending on the  $\text{Sr}^{2+}_{(\text{aq})}$  concentration. Among the observations was the so-called “template effect” at low  $\text{Sr}^{2+}_{(\text{aq})}$  concentrations (~0.2 mM), where monolayer growth is affected by the previously-grown underlayer and, at higher  $\text{Sr}^{2+}_{(\text{aq})}$  concentrations (~2 mM), growth is followed by dissolution and precipitation of 3-D nuclei. Wasylenki et al. (2005) performed a detailed AFM study on the effect of Sr on spiral growth of calcite at low supersaturation. Their experiments were conducted with smaller  $\text{Sr}^{2+}_{(\text{aq})}$  concentrations and smaller  $\text{Sr}^{2+}_{(\text{aq})}/\text{Ca}^{2+}_{(\text{aq})}$  ratio, as compared to those from Astilleros et al. (2003a). Wasylenki et al. (2005) found that calcite growth was brought to a complete halt once a certain value of  $\text{Sr}^{2+}_{(\text{aq})}$  concentration was achieved in the growing solution. This threshold concentration varied as a function of supersaturation. Additionally, they performed segregation experiments on growth hillocks at low  $\text{Sr}^{2+}_{(\text{aq})}$  concentrations (0.05 mM) and low  $\text{Sr}^{2+}_{(\text{aq})}/\text{Ca}^{2+}_{(\text{aq})}$  ratios (0.19) and found preferential incorporation of Sr in the obtuse growth sector, verifying the observations made by Paquette and Reeder (1995). More recently, Bracco et al. (2012) found in their AFM investigations of Sr-calcite

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growth that the total inhibition of growth due to  $\text{Sr}^{2+}_{(\text{aq})}$  correlated with the  $\text{Ca}^{2+}_{(\text{aq})}$  concentration, but not the carbonate concentration, suggesting that Sr inhibition occurred by blocking Ca attachment.

It has been shown in the past decade that friction force microscopy (FFM) can provide contrasting information on chemically-distinct surface overgrowths of nanometer thickness and at high lateral resolution (therefore, surpassing to some extent traditional surface analytical techniques such as X-ray Photoelectron Spectroscopy and Energy Dispersive X-ray analysis). With the ability to detect differences in composition at the nanometer scale, FFM may reveal new detail on the microstructure and chemistry of compositional boundaries in sedimentary minerals. For example, Hay et al. (2003) showed an increase in the lateral force signal for metal-bearing carbonates, including Sr, growing over a pure calcite substrate. Higgins and co-workers (Higgins and Hu, 2005; Higgins et al., 2007; Hu et al., 2010) reported friction differences, in aqueous solution, associated with non-stoichiometric dolomite overgrowths whereby Ca-rich films displayed increased friction over the native dolomite surface. Cubillas and Higgins (2009) performed a more detailed study on the friction change of cadmium–calcium carbonate overgrowths of different compositions and demonstrated that FFM could detect very small compositional differences (5–10% in Cd content) on calcite growth in the presence of  $\text{Cd}^{2+}_{(\text{aq})}$ .

In this paper we present results from the study of Sr partitioning in calcite growth experiments by means of FFM. In an effort to assess the sensitivity of FFM to Sr levels in growing calcite, these experiments were designed to examine conditions under which Sr–calcite growth is self-limiting (e.g., the so-called “template effect”) and also to investigate continuous Sr–calcite growth conditions, where spiral growth predominates. As shown in previous work by Paquette and Reeder (1995) and Wasylenki et al. (2005), Sr is preferentially incorporated into obtuse steps on calcite (104) surfaces. An additional objective of the current investigations is to evaluate the utility of FFM for observing this specific type of sector zoning in calcite, where differences in the overgrowths' chemical composition are expected to be very small.

## 2. Materials and methods

### 2.1. Experimental Set up

Experiments were performed at room temperature ( $25 \pm 2$  °C) using a custom-built AFM (Higgins et al., 1998) equipped with a closed flow cell and interfaced to an Agilent (Molecular Imaging) PicoScan 2500 SPM controller. The flow cell was designed to produce a vertically impinging solution jet onto the sample surface and laterally displaced by 2 mm from the tip/surface contact (Bose et al., 2008). All experiments were performed in contact mode using silicon cantilevers (Point Probe Plus-CONT). In some experiments, cantilever load was varied in order to observe its effect on the change of friction signal from the different overgrowths. Load was calculated using the deflection signal from the free position of the cantilever as the zero load point. Calibration of the load applied and friction force signal was carried out following the procedure described in detail in Cubillas and Higgins (2009).

Fresh calcite samples were prepared by cleaving optically clear Iceland Spar crystals (Ward's Natural Science Est. Inc.) along the (10  $\bar{1}$  4) plane using a razor blade. Minor and trace chemical analyses of crystals from the same batch are reported in Xu et al. (2010). Typical sizes of the cleaved crystals were approximately 5 mm  $\times$  5 mm  $\times$  1 mm. Samples were mounted into the fluid cell immediately after cleavage to prevent contamination. Prior to the start of the experiment, a calcite-undersaturated solution of  $\text{CaCl}_2$  (0.3 mM) and  $\text{NaHCO}_3$  (0.3 mM) (pH = 7.5–8) was flushed through the cell to promote slow dissolution of the calcite sample and to generate etch pits. Afterwards, a solution containing the desired ion combinations was introduced. The total duration of the experiments varied between 2 and 20 h. For experiments

Sr–calcite.1 to Sr–calcite.3 zoomed out scans were performed after the relevant scans were performed in order to evaluate possible tip-modified topography. These larger-scale images (not shown) revealed that there was no tip scanning effect on the observed results. Fluid flow rate was maintained constant to  $2.5 \pm 0.1$  g/h using a Porter Instrument mass flow controller.

Solutions were prepared using de-ionized water (18 M $\Omega$ -cm resistivity), and high-purity  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NaHCO}_3$ ,  $\text{SrCl}_2$ , and  $\text{NaOH}$ . pH adjustment of the inlet solutions was achieved by adding small amounts of a  $\text{NaOH}$  solution (0.1 mol/L) to the initial solution. Once the desired pH was achieved, the solution was injected into the flow system by means of a 20 mL syringe. Re-equilibration kinetics of these solutions with  $\text{CO}_2$  under the pH ranges used (8–9.5) were slow, so the pH measured just before introducing the solution into the  $\text{CO}_2$ -free flow system was considered to be the pH of the solution in the flow cell where the calcite sample was located. pH measurements were carried out using an Accumet® pH/ATC Combination electrode (Fisher Scientific 1961/Accumet) connected to a dual ion/pH meter from Fisher Scientific. The pH electrode was calibrated using pH 4, 7, and 10 standard buffer solutions from Fisher Scientific.

### 2.2. Solid solution theory and saturation calculation

It is well known that  $\text{SrCO}_3$  possesses an aragonite-type orthorhombic structure. Nevertheless, several authors have suggested that Sr can be incorporated into the structure of calcite (Astilleros et al., 2003; Hay et al., 2003; Paquette and Reeder, 1995; Pingitore and Eastman, 1986; Wasylenki et al., 2005). Astilleros et al. (2003a) developed the thermodynamics of the Calcite– $\text{SrCO}_3$ (<sub>rhomb</sub>) solid solution (SS). Because a rhombohedral  $\text{SrCO}_3$  phase has never been observed nor experimentally precipitated, they calculated its solubility product using a theoretical approach, obtaining a value of  $10^{-7.55}$ . By taking into account the thermodynamics of the calcite– $\text{SrCO}_3$ (<sub>rhomb</sub>) and aragonite–strontianite solid solutions Astilleros et al. (2003a) calculated a stability diagram for the whole Sr–Ca compositional range, where it was found that for an aqueous mole fraction of Sr ( $X_{\text{Sr, aq}}$ ) of less than 0.125 the mineral with a calcite structure was the most stable, whereas for higher  $\text{Sr}^{2+}_{(\text{aq})}$  content the thermodynamically-favored phase had the aragonite type structure. They also predicted the existence of a miscibility gap between  $0.15 < X_{\text{Sr, aq}} < 0.875$  for the aragonite–strontianite system.

Activities and saturation indices of the solutions were calculated using the program PHREEQC (Parkhurst and Appelo, 1999) and the PHREEQC database. Saturation index is defined as:

$$SI = \log \left( \frac{IAP}{K_{sp}} \right) \quad (1)$$

where  $IAP$  is the ion activity product and  $K_{sp}$  is the solubility product of the solid phase. The saturation state of a solid solution (B,C)A is not represented by a single value but is a function of both the solid and aqueous phase compositions. The general expression of the supersaturation function has the form (Prieto et al., 1993):

$$\beta(X) = \frac{[B^+]^X [C^+]^{(1-X)} [A^-]}{(K_{BA} \cdot \gamma_{BA} \cdot X_{BA})^X (K_{CA} \cdot \gamma_{CA} \cdot X_{CA})^{(1-X)}} \quad (2)$$

where  $[A^-]$  refers to the activity of ion  $A$  in the aqueous solution,  $K_{BA}$  refers to the solubility product of the  $BA$  end-member,  $X_{BA}$  is the mole fraction,  $\gamma_{BA}$  is its activity coefficient and  $X = X_{BA}$ . The maximum of the supersaturation function provides a good approximation of the precipitating solid-solution composition; nevertheless it does not take into account the kinetics of the nucleation process. More accurate predictions of the composition of the precipitating solid-solution requires this latter consideration (with the knowledge of a number of experimental parameters) as has been shown (Pina et al., 2000). The saturation states for the different solid solution compositions were

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