

# Calcite crystal growth orientation: implications for trace metal uptake into coccoliths

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## ABSTRACT

Inorganic calcite precipitation experiments were conducted to determine whether inducing specific orientations of calcite crystal growth can cause the enrichment of cations larger than Ca. Malonic acid ( $\text{CH}_2(\text{COOH})_2$ ), a di-carboxylic acid, was used to poison growth on acute kink sites, promoting growth on obtuse kink sites, causing calcite crystals elongated along their *c*-axes to form in a mechanism similar to that seen in the growth of *E. huxleyi* coccoliths. Calcite was precipitated with a range of malonic acid concentrations (0 to  $10^{-1}$  M), and  $9 \times 10^{-5}$  M of either  $\text{SrCl}_2$  or  $\text{MgCl}_2$ . The results show that calcite crystals precipitated in the presence of large malonic acid concentrations show significant elongation along the *c* axis, and suggest that increasing malonate concentrations corresponded with increasing  $D_{\text{Sr}}$ . Experiments with  $10^{-1}$  M malonic acid caused elevated  $D_{\text{Sr}}$  comparable to that predicted for *E. huxleyi* coccolith calcite (Langer *et al.*, 2006).

## Introduction

COCCOLITHOPHORIDS are a significant group of unicellular calcifying organisms in the world's oceans. The production of tiny, but intricate, calcite scales (coccoliths) by these organisms allows coccolithophorids to wield considerable influence over global biogeochemical cycles, such as the global carbon cycle. Coccolith calcite exhibits considerable inter-species variation in trace element (e.g. Sr/Ca) and stable isotopic ratios (e.g.  $\delta^{18}\text{O}$ ). Recent studies have attempted to develop novel geochemical proxies, linking the geochemical signature of coccolith calcite with specific environmental parameters such as ocean productivity, although determining precise controls over coccolith calcite geochemistry has proved difficult (e.g. Rickaby *et al.*, 2007). Coccolith calcification occurs intracellularly, within specialist vesicles (Van der Wal *et al.*, 1983) where growth is initiated as a protococcolith ring. Larger calcite single crystals grow from this ring to form the coccolith (Young *et al.*, 1992). The dominant extant bloom species,

*Emiliania huxleyi*, consists almost solely of radially aligned (R) calcite, which has been found to display elevated Sr/Ca ratios when compared to inorganic calcite (Rickaby *et al.*, 2007). The radial alignment of *E. huxleyi* coccolith calcite has been suggested to develop by the propagation of obtuse kink sites on the  $\{10\bar{1}4\}$  surface of calcite, promoting growth parallel to the *c* axis, this process is believed to occur via the blocking of acute kink sites by coccolith associated polysaccharide (CAP, Henriksen *et al.*, 2004). Cations such as Sr (atomic radii larger than Ca) seem to become preferentially incorporated into obtuse kink sites during the growth of inorganic calcite crystals (Paquette and Reader, 1995). We hypothesize that carboxylic-bearing additives which mimic the behaviour of CAP by blocking the acute surface kink sites cause the enrichment of larger ions, such as Sr, and a depletion of smaller ions, such as Mg, in calcite. In this study inorganic calcite growth experiments were used to test this hypothesis. The radial *c*-axis growth of calcite crystals was promoted using malonic acid ( $\text{CH}_2(\text{COOH})_2$ ), a di-carboxyl-bearing organic acid additive, to mimic the interaction of CAP with the growing calcite (e.g. Mann *et al.*, 1990).

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Results indicate that elongation along the  $c$  axis and Sr partition coefficient  $D_{Sr}$  increases with malonate concentration.

## Methods

The method used, based on that developed by Tesoriero and Pankow (1996), facilitated the precipitation of calcite while achieving equilibrium fractionation of the incorporated trace metal (either Sr or Mg). Calcite growth was initiated by continuous slow pumping of 50 ml each of 0.5 M  $\text{Na}_2\text{CO}_3$  and 0.5 M  $\text{CaCl}_2$  from a dual syringe pump into 1 litre of 0.22 M NaCl background electrolyte, already equilibrated with a calcite seed growth substrate (sieved to 45–63  $\mu\text{m}$ ). Once a constant calcite precipitation rate was reached (determined by achieving constant pH level of  $\sim 8.3$ ), 1 ml of 0.09 M  $\text{SrCl}_2$  or  $\text{MgCl}_2$  was added and malonic acid to give a total concentration between 0 and  $10^{-1}$  M in the suspension. Precipitation was terminated after a specified time (48 or 96 h) by cessation of pumping. Two solution samples were collected, one directly after initiation of pumping ( $T_1$ ) and another immediately after cessation of pumping ( $T_2$ ). The solutions were syringe filtered, and immediately acidified with pure nitric acid. Solid calcite samples were collected using a vacuum filtration unit. The solids were rinsed with a  $\text{CaCO}_3$  saturated solution to remove any salt residues, then dried for 24 h at  $105^\circ\text{C}$ . The morphologies and mineralogy of the resulting solids were characterized using scanning electron microscopy (SEM) and powder X-ray diffraction (XRD). Trace metal and Ca concentrations of the solid calcite samples (after dissolution

in nitric acid) and the supernatant were determined using inductively coupled plasma mass spectrometry (ICP-MS).

Throughout the experiment the reagents were added continuously and thus the components removed during  $\text{CaCO}_3$  precipitation were continuously balanced. The partition coefficient,  $D_{Sr}$ , was calculated following the Henderson-Kracek (1927) equation for homogenous co-precipitation:

$$D_{Sr} = \frac{[\text{Sr}/\text{Ca}]_{\text{Calcite}}}{[\text{Sr}/\text{Ca}]_{\text{Solution}}}$$

where  $[\text{Sr}/\text{Ca}]_{\text{Calcite}}$  is the Sr to Ca molar ratio in the calcite precipitated between the initial solution sample ( $T_1$ ) and the final solution sample ( $T_2$ ).

## Results and discussion

Our results indicate that calcite crystal elongation along the  $c$  axis and Sr partition coefficient ( $D_{Sr}$ ) increase with malonate concentration. Calcite crystals grown in the absence of malonic acid additive formed roughly equant intergrown rhombs, due to the aggregated nature of the seed material used (Fig. 1a). Experiments with calcite grown with increasing concentrations of malonic acid additive produced progressively more pronounced elongation of calcite crystals along the  $c$  axis (Fig. 1b). Calculated  $D_{Sr}$  are shown in Fig. 2. Experiments conducted in the absence of malonic acid growth modifier produced calcite with a  $D_{Sr}$  close to that determined for pure inorganic calcite, i.e. 0.021 (Tesoriero and

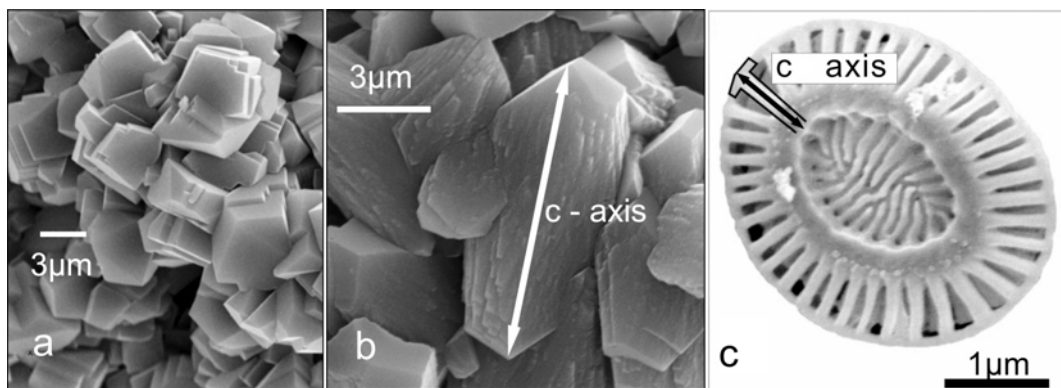


FIG. 1. SEM images of (a) calcite grown in the absence of growth modifiers; (b) calcite grown with  $10^{-2}$  M malonic acid, showing the orientation of the  $c$  axis; and (c) *Emilia huxleyi* coccolith, showing the orientation of the  $c$  axis.

## CALCITE CRYSTAL GROWTH ORIENTATION

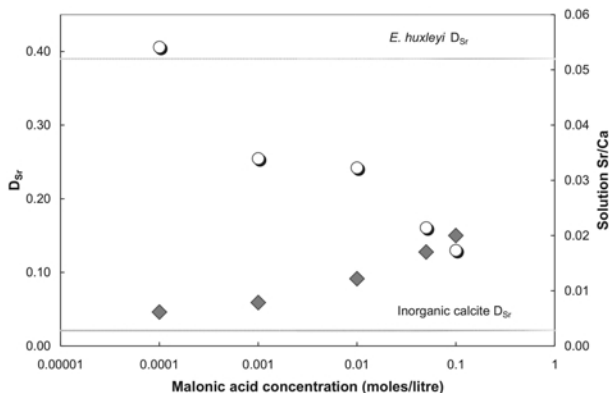


FIG. 2.  $D_{Sr}$  (grey diamonds) and final solution Sr/Ca concentration (open circles) compared to malonic acid concentration. *E. huxleyi*  $D_{Sr}$  predicted by Langer *et al.* (2006), inorganic calcite  $D_{Sr}$  as expected from Tesoriero and Pankow (1996).

Pankow, 1996). As the concentration of malonic acid additive increased the  $D_{Sr}$  increased. The largest concentration of malonic acid ( $10^{-1}$  M) produced calcite with a  $D_{Sr}$  of 0.130, which is approaching the  $D_{Sr}$  of 0.39 estimated by Langer *et al.* (2006) for *E. huxleyi* coccolith calcite. As malonic acid concentration increased the concentration of Sr remaining in the solution decreased. Conversely, the concentration of Mg remaining in solution decreased with increasing malonate concentration, suggesting that the Mg concentration of the calcite decreases with increasing malonate.

The data show that increasing the concentration of malonic acid caused increased partitioning of Sr into calcite crystals. Since precipitation rates for each experiment were similar, and within the threshold where  $D_{Sr}$  remains constant with

varying growth rate in inorganic systems (Tesoriero and Pankow, 1996), it seems that this increased Sr partitioning into the crystal cannot be due to changes in calcite precipitation rate (Fig. 3). It seems certain, therefore, that the increase in  $D_{Sr}$  is due to the presence of increasing concentrations of malonic acid growth modifier. Carboxylic acids can affect calcite growth because of the similarity of the carboxyl ( $\text{COO}^-$ ) group to the carbonate group ( $\text{CO}_3^{2-}$ ), allowing it to interact with Ca ions at the calcite surface through electrostatic attraction. The bidentate binding of the carboxyl groups of dicarboxylic acids to the calcite surface can effectively block acute kink sites (Mann *et al.*, 1990) allowing growth only on obtuse sites. If growth predominantly occurs on obtuse kink sites, larger cations such as Sr are preferentially

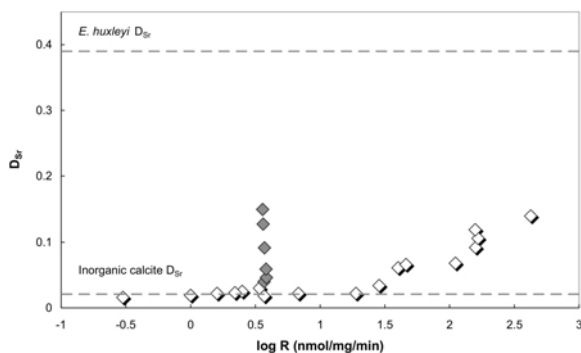


FIG. 3.  $D_{Sr}$  results from this study (grey diamonds) and for inorganic calcite compared to precipitation rate (Tesoriero and Pankow, 1996; open diamonds).

incorporated into the crystal lattice (Paquette and Reader, 1996). The  $D_{Sr}$  and final solution concentrations of Sr and Mg seem to support this hypothesis, since if growth occurs predominantly on obtuse kink sites it is expected that large cations such as Sr will be preferentially incorporated into the calcite crystal lattice. Also, smaller cations such as Mg will be preferentially retained in solution. The growth modification tested in this study is likely to occur by the same mechanism suggested by Henriksen *et al.* (2004) for CAP associated calcite growth to form radially aligned *E. huxleyi* coccolith calcite. *E. huxleyi* CAP bears numerous carboxyl groups which can block acute kink sites. The experiments in this study using  $10^{-1}$  M malonic acid produced elongate calcite with an elevated  $D_{Sr}$ . It therefore seems feasible that Sr enriched *E. huxleyi* coccolith calcite could be produced by the interaction of CAP with the growing coccolith calcite. However, in order to fully quantify the processes causing Sr enrichment in coccolith calcite the Sr/Ca of the intracellular fluid within the coccolithophore vesicle needs to be known.

## Conclusion

Malonic acid is an effective growth modifier of calcite, causing elongation of the calcite crystal along the *c* axis. Concomitant with this elongation, Sr is preferentially removed from solution, while with increasing malonic acid concentrations Mg increasingly remains partitioned in the solution phase. These results support the tested hypothesis, and suggest that Sr enriched *E. huxleyi* coccolith calcite is not necessarily formed due to the high growth rates of the organism, but are caused, at least in part, by the interaction of carboxyl-bearing *E. huxleyi* CAP with the growing coccolith calcite.

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