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I am submitting herewith a thesis written by Emily Elizabeth Goodman entitled “Laboratory precipitation and geochemical investigation of unstable CaCO_3 polymorphs: Implications for the origin of Precambrian “molar-tooth” microspar.” I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.

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**Laboratory precipitation and geochemical investigation of
unstable CaCO_3 polymorphs: Implications for the origin of
Precambrian “molar-tooth” microspar**

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Degree
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Abstract

Molar-tooth (MT) microspar is a volumetrically significant, globally distributed carbonate fabric that occurs almost exclusively in Mesoproterozoic and early Neoproterozoic shallow marine successions. It occurs as uniform, equant crystals, averaging 9–15 μm in diameter (Figure 1), that characteristically fill MT structures—interconnected networks of spheroidal, spindle, and ribbon-shaped voids that formed within unlithified sediment in shallow, subtidal environments. Cathodoluminescence (CL) analysis of MT microspar reveals two chemically distinct phases: a dullly luminescent spheroidal core enclosed by a luminescent, polygonal rim. Crystal size distribution analysis of MT microspar indicates spontaneous nucleation, rapid growth and varying degrees of recrystallization by Ostwald ripening, followed by precipitation of overgrowth cements. Petrographic and isotopic characteristics suggest MT microspar is a primary precipitate and not a diagenetic or neomorphic phenomenon and that precipitation occurred in active communication with Proterozoic seawater. Therefore, constraining the genesis of MT microspar is critical to understanding the geochemical evolution of Proterozoic seawater.

Morphological similarities have led to comparisons between MT microspar and experimentally precipitated vaterite, a metastable CaCO_3 polymorph. Presented here are results of precipitation experiments designed to investigate the plausibility of vaterite as the precursor mineralogy to MT cores, and to explore the geochemical conditions under which MT microspar may have formed. Any hypothesis for the formation of MT microspar must account for the crystal size and morphologies observed in MT microspar cores, as well the volume of precipitate needed to fill and

stabilize MT structures. These experiments show that (1) spheroidal morphologies are common in both vaterite and calcite, suggesting that MT microspar may have initiated as a polymineralic precipitate and (2) that even under greatly elevated saturations, insufficient precipitate is produced to account for observed volumes of MT microspar. Experiments performed at elevated pH with added Mg^{2+} , however, produced a viscous colloid, suggesting that under conditions of high carbonate saturation an amorphous phase of significant volume may have filled, and thus stabilized, MT structures in the unlithified substrate.

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**PART I: Experimental vaterite precipitation as an analog
study of Precambrian molar-tooth microspar**

1. Introduction

The Precambrian sedimentary record is characterized by a variety of unusual carbonate morphologies, many of which appear to have precipitated from marine waters highly supersaturated with respect to calcium carbonate (Grotzinger, 1989; Grotzinger and Kasting, 1993). These morphologies, which are rarely found in Phanerozoic marine deposits, include accumulations of large seafloor-precipitated fibrous calcite and aragonite fans not associated with any fine-grained micrite production (Sumner and Grotzinger, 1996a); microlaminated crystalline crusts that dominate stromatolites fabrics and encrust the seafloor (Knoll and Swett, 1990; Grotzinger, 1990; Kah and Knoll, 1996; Sumner and Grotzinger 1996a; Bartley et al., 2000); herringbone carbonate, a cement and seafloor precipitate whose unusual curved crystal growth habit has been attributed to either inhibition by ferrous iron concentrated in anoxic oceans (Sumner and Grotzinger, 1996b) or rapid growth in the presence of high dissolved organic carbonate (DOC) (Tourre and Sumner, 2000); and molar-tooth (MT) microspar, a spheroidal precipitate that characteristically formed at or near sediment–water interface (Furniss et al., 1998; Pollock et al., 2006; Bishop et al., 2006a,b). The gradual decline and eventual disappearance of these types of precipitates is attributed to long term changes in the carbonate saturation state of the marine system (Sumner and Grotzinger, 1996a,b; Grotzinger, 1990; Kah and Knoll, 1996; Bartley et al., 2000), possibly linked to a decrease in atmospheric $p\text{CO}_2$ and concomitant decline in marine dissolved inorganic carbon (DIC) (Grotzinger, 1990; Grotzinger and Kasting, 1993; Shields, 2002; Bartley and Kah, 2005). Identification

of the chemical conditions that controlled the formation of these unusual carbonate morphologies is therefore critical to understanding changes in ocean-atmosphere chemistry throughout the Precambrian.

Of these morphologies, MT microspar occurs almost exclusively in Mesoproterozoic and early Neoproterozoic shallow marine successions (James et al., 1998; Shields, 2002; see Bishop et al., 2006a,b for a reported Archaean occurrence). MT microspar is a volumetrically significant, globally distributed carbonate fabric that occurs as uniform, equant crystals, averaging from 9-15 μm in diameter (Figure 1), that characteristically fill MT structures. MT structures (Figure 2) occur as an interconnected network of spheroidal, spindle, and ribbon-shaped veins that formed within unlithified sediment in subtidal environments (James et al., 1998), perhaps extending as deep as storm wave base (Pratt et al., 1998, 2001; Bishop et al., 2006b). Several mechanisms for MT void genesis have been proposed, including subaqueous sediment compaction (Bell, 1966), destabilization of methane clathrates (Marshall and Anglin, 2004), replacement of algal structures (O'Conner, 1972; Moussine-Pouchkine and Bertrand Sarfati, 1997) and tectonically induced sediment dewatering (Fairchild et al., 1997; Pratt, 1998, 2001). The most compelling evidence, however, implicates the migration of gas derived from microbial decomposition of organic matter within unlithified sediments (Furniss et al., 1998; Pollock et al., 2006).

Although the genesis of void formation remains controversial, several observations indicate that microspar precipitation occurred rapidly and penecontemporaneously with void formation and suggest that voids and void-filling microspar share a common origin (Furniss et al. 1997; Frank et al. 1997; Lyons

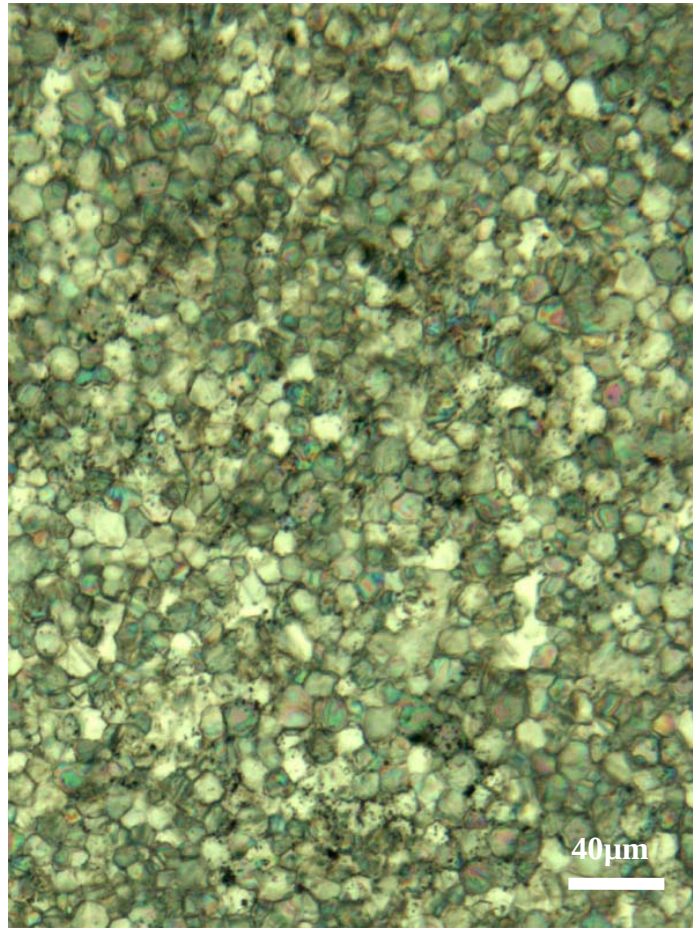


Figure 1. Transmitted light photomicrograph of MT microspar, exhibiting 5-15 μm clear, equant, non-interlocking crystals that share planar boundaries. Photo from Crawford (2005)



Figure 2. MT structures from the Mesoproterozoic Kataskin Formation, Avzyan Supergroup, Russia. Sediment laminae are both crosscut by and compacted around microspar-filled voids.

et al., 2005; Pollock et al. 2006). Sediment laminae compacted around microspar-filled voids, microspar-filled voids extending above local scour surfaces, and intraclasts of microspar found as reworked lag deposits suggest that crack formation and microspar precipitation and lithification occurred prior to compaction and lithification of surrounding substrate (Pratt, 1998; Furniss et al. 1998; James et al., 1998). Furthermore, although MT microspar does not exhibit the characteristics common to most typical carbonate cements, such as competitive growth or coarsening-inward crystal morphologies, neither do they exhibit characteristics of neomorphosed carbonates. Rather, MT microspar characteristically displays clear, equant, non interlocking crystals that share planar boundaries. They are not preferentially oriented and show a sharp contact with surrounding matrix (Figure 3). Combined, these petrologic features suggest precipitation of MT microspar as a primary precipitate within MT structures.

Cathodoluminescence (CL) analysis of MT microspar reveals that each crystal contains a dullly luminescent, typically spheroidal core enclosed by a luminescent, polygonal rim (Figure 4a) (Crawford and Kah, 2005; Pollock et al., 2006; Bishop et al., 2006b) and supports the interpretation of microspar formation as an in situ precipitate. Analysis of crystal size distributions (CSDs) indicates that cores formed in a single nucleation event, followed by rapid initial growth and various degrees of Ostwald ripening (Crawford, 2006). Although cores are most commonly spheroidal, a range of morphologies spanning transitional subhedral to euhedral rhombic cores are also observed (Figure 4b). Crawford (2006) interpreted crystal size distributions and variable core shapes as evidence of the unstable nature of initial core

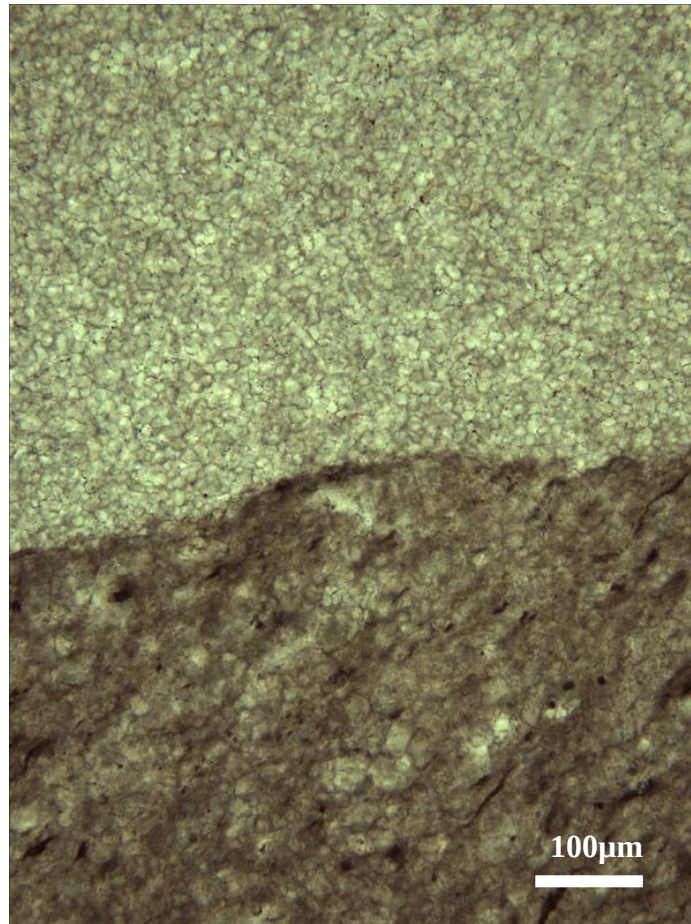


Figure 3. Transmitted light photomicrograph of sharp contact between MT microspar (top) and surrounding matrix. From Crawford (2005)

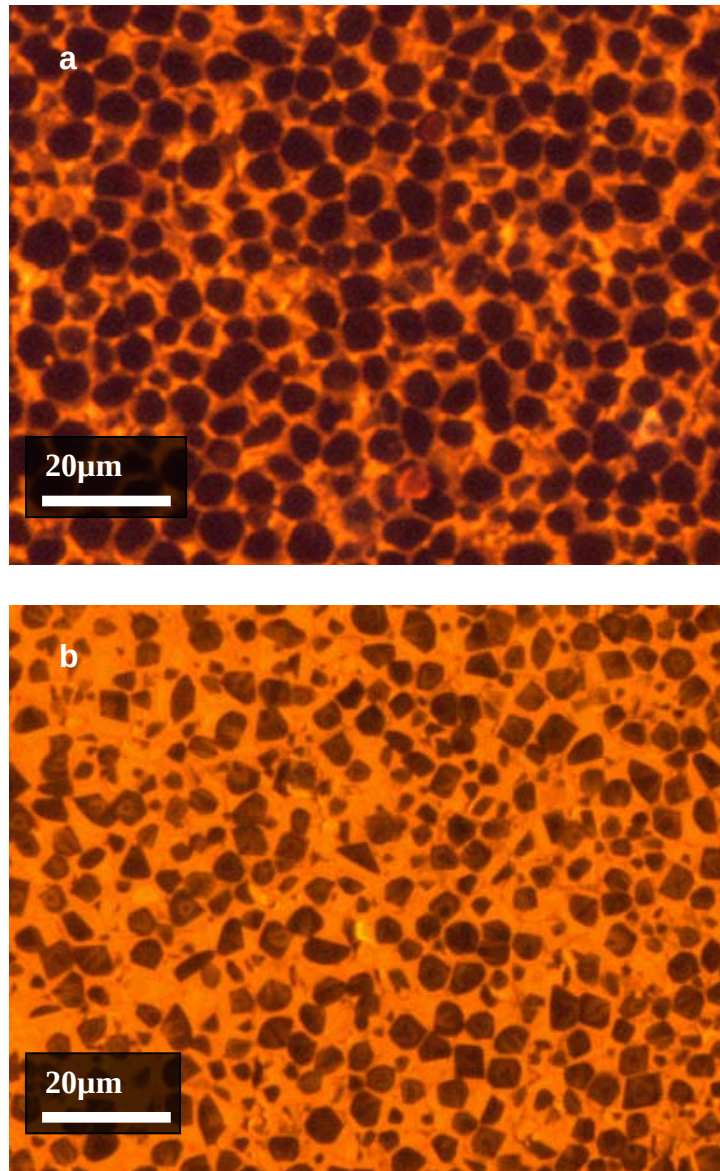


Figure 4. Cathodoluminescent photomicrographs of MT microspar showing dully luminescent cores surrounded by luminescent, polygonal overgrowth cements. (a) Dominantly spheroidal cores are unzoned, suggesting primary precipitate. (b) Zoned, rhombic cores suggesting recrystallization in pore fluids. From Crawford (2005).

mineralogy and proposed a three-stage growth history: 1) spontaneous nucleation and growth followed by Ostwald ripening, 2) transformation of some crystals to rhombic morphologies by dissolution and reprecipitation and 3) restriction of further morphologic transformation and filling of void space between cores by precipitation of overgrowth cements.

Based on petrographic relationships between microspar and associated MT structures, Pollock et al. (2006) developed a model for MT genesis that illustrated how the migration of gas within unlithified sediments of varying cohesive strength could produce both predictable void morphologies and immediate precipitation of MT microspar. In this model migration of gas derived from microbial decomposition in the shallow subsurface would result in pore fluids with elevated concentrations of both DIC and a variety of dissolved organic molecules; when migrating pore fluids came into contact with supersaturated Proterozoic marine seawater, rapid precipitation of void-filling microspar would occur. Carbon isotope analyses of MT microspar show little deviation in $\delta^{13}\text{C}$ values from associated, coeval marine carbonates (Frank et al., 1997; Frank and Lyons, 1998; Pope et al., 2003; Marshall and Anglin, 2004, Crawford, 2005; Bishop et al., 2006a), indicating that seawater is the dominant source for CO_3^{2-} in the void filling cement (Frank and Lyons, 1998; Pope et al., 2003) and suggesting that the influence of any organically-derived carbon from sulfate reduction or methanogenesis is overwhelmed by this seawater signature (Frank and Lyons, 1998; Lyons et al., 2005; Bishop et al., 2006a).

Pollock et al. (2006) described an oolitic grainstone from the ~1.45 Ga Helena Formation, Belt Supergroup, Montana, USA, in which MT microspar is the primary

intergranular component, suggesting a scenario where gas and fluid escape may have driven rapid precipitation of MT microspar in the overlying water column. In another example, Bartley and Kah (2007) described MT microspar as a primary component in a series of amalgamated, fluidized beds in the ~1.2 Ga Tawaz Formation, Atar Group, Mauritania. Combined, these lines of evidence indicate that MT microspar formed in active communication with Proterozoic ocean water.

Based on petrographically uniform grain size, Gellatly and Winston (1998) proposed that MT microspar initially precipitated as vaterite, a hexagonal metastable calcium carbonate polymorph that rapidly transforms to calcite in solution (Kralj et al., 1997). Subsequent investigations have revealed additional similarities between Precambrian MT microspar and laboratory–precipitated vaterite. Spheroidal crystals that compose the cores of MT microspar are commonly associated with vaterite precipitation at either highly elevated carbonate saturations or in the presence of a variety of dissolved organic molecules (Naka and Chujo 2001; Kralj et al. 1994, 1997; Sawada et al. 1990). Rapid nucleation and growth, Ostwald ripening, and immediate morphological and mineralogical transformation, as described by Crawford (2006), is also consistent with laboratory experiments wherein vaterite precipitation is rapidly followed by recrystallization and stabilization (Kralj et al., 1998). Finally, SIMS ion imaging suggests that spheroidal cores of MT microspar are enriched in Mg^{2+} , with concentrations possibly exceeding those of high-Mg calcite (Crawford 2005). Enrichment in Mg^{2+} is consistent with an originally vaterite mineralogy, which has been found to incorporate high concentrations of Mg^{2+} into its

crystal structure (Sawada et al. 1990). Combined, these lines of evidence support vaterite as a likely precursor to MT microspar.

The goal of this study is to further explore the role of vaterite as a possible precursor to molar-tooth microspar. Specifically, I have used a series of laboratory precipitation experiments to: 1) determine the geochemical conditions under which vaterite is most likely to form, 2) determine whether experimentally precipitated vaterite exhibits the range of crystal size and shape observed in MT microspar cores, and 3) determine whether a volume of precipitate comparable to that required to fill MT voids can be produced experimentally. Together these determinations will aid in the development of a detailed geochemical framework in which to examine the long-term distribution of MT microspar in the Proterozoic.

2. Methods

2.1. Experimental procedure

Reactions were carried out at room temperature (20°C) in a modified Erlenmeyer flask that allows for reagent input and aliquot withdrawal through rubber septa without opening the system to the ambient atmosphere (Figure 5). All reactants used in the precipitation experiments were reagent grade. Reactant solutions, excluding Ricca brand synthetic seawater, were prepared using Millipore Milli-Q water.

For each experiment, a calcium source solution was added to the Erlenmeyer flask. Molar concentrations reported here represent the concentration of each species in the total reaction solution (see Appendix A, Table A.1, for reactant concentrations prior to mixing). The Ca^{2+} source solutions, in concentrations ranging from 0.01 – 0.03 M Ca^{2+} , were made by mixing crystalline calcium chloride (CaCl_2) or calcium acetate [$\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$] in a variety of solvents (see Table 1). The combinations of Ca^{2+} sources and solvents were: 1) CaCl_2 with Ricca brand synthetic seawater, 2) CaCl_2 with Milli-Q water, 3) CaCl_2 with Milli-Q water adjusted to the ionic strength of seawater ($I = 0.7$) using crystalline NaCl, 4) calcium acetate with Milli-Q water, and 5) calcium acetate with Ricca brand synthetic seawater. The flask was then flushed with nitrogen gas to remove atmospheric gases and capped with a rubber stopper fitted with a pH electrode.



Figure 5. Experimental vessel with immersed pH electrode allowed for reactant input and aliquot withdrawal without exposure to the ambient atmosphere.

Table 1. Reactant concentrations, precipitate volumes, and mineralogy of carbonate precipitation experiments.

Solute + CO ₃ ²⁻ source	Total reactant concentrations (moles/L)	Time (minutes)	Volume precipitate (%/mL)*	Percent vaterite	Percent calcite	Added trace element concentration
<i>Synthetic seawater + Na₂CO₃</i>						
	0.1	5	0.26	0	100	
	0.3	10	1.50	0	100	
<i>NaCl₂ solution (I=0.7) + Na₂CO₃</i>						
	0.01	5	0.05	33.1	66.9	
	0.03	5	0.27	26.7	73.3	
	0.03	20	0.27	14.2	85.8	
	0.06	5	0.60	22.1	77.9	
	0.06	20	0.52	12.8	87.2	
	0.1	2.5	0.98	59.3	40.7	
	0.1	5	0.94	57.1	42.9	
	0.2	5	1.53	85	15	
	0.2	5	1.91	87.4	12.6	
	0.25	5	2.32	85.2	14.8	
<i>Milli-Q water + Na₂CO₃</i>						
	0.2	5	1.83	84.9	15.1	
	0.2	5	1.86	77.8	22.2	
	0.2	15	1.83	79.7	20.3	
	0.2	10	1.83	77.6	22.4	
	0.2	15	1.76	63.9	36.1	
	0.25	5	2.36	71.3	28.7	
<i>Milli-Q water + Na₂CO₃ + Mg²⁺</i>						
	0.2	5	Unknown**	0	100	53.2 mM Mg ²⁺
	0.2	5	Unknown**	0	Unknown**	108.4 mM Mg ²⁺
	0.2	5	Unknown**	0	Unknown**	266 mM Mg ²⁺
<i>Milli-Q water + NaHCO₃</i>						
	0.1	5	0.26	90	10	
	0.15	5	0.39	94.2	5.8	
	0.2	5	0.60	94.5	5.5	
	0.2	5	0.65	93.7	6.3	
	0.2	5	1.30	95.8	4.2	
	0.2	10	0.66	86.9	13.1	
	0.2	10	0.77	90.5	9.5	
	0.2	15	0.81	80.2	19.8	
	0.25	5	0.93	93.8	6.2	
	0.3	5	1.21	92.5	7.5	
<i>Milli-Q water + NaHCO₃ + Mg²⁺</i>						
	0.2	5	0.51	86.3	13.7	53.2 mM Mg ²⁺
	0.2	5	0.51	84.8	15.2	53.2 mM Mg ²⁺
	0.2	5	0.26	66.7	33.3	108.4 mM Mg ²⁺
	0.2	5	0.23	67.5	32.5	108.4 mM Mg ²⁺
	0.2	5	0.10	78.2	21.8	266 mM Mg ²⁺
	0.2	5	0.09	0	100	266 mM Mg ²⁺

Table 1. Continued.

Solute + reactant type	Total reactant concentrations (moles/L)	Time (minutes)	Volume precipitate (%/mL)*	Percent vaterite	Percent calcite
<i>Synthetic seawater + Na₂CO₃ + Calcium acetate</i>					
	0.1	5	0.97	10.9	89.1
	0.1	10	0.93	7.1	92.9
	0.2	5	2.03	72.3	27.7
	0.2	10	1.98	69.3	30.7
<i>Milli-Q water + Na₂CO₃ + Calcium acetate</i>					
	0.1	5	0.95	84.4	15.6
	0.1	10	0.91	82.3	17.7
	0.2	5	1.83	96.7	3.3
	0.2	10	1.93	93.1	6.9
<i>Synthetic seawater + NaHCO₃ + Calcium acetate</i>					
	0.1	5	0.05	14.5	85.5
	0.1	10	0.06	10.1	89.9
	0.2	5	0.60	91.5	8.5
	0.2	10	0.79	97.6	2.4
<i>Milli-Q water + NaHCO₃ + Calcium acetate</i>					
	0.1	5	0.32	98.1	1.9
	0.1	10	0.36	97.5	2.5
	0.2	5	0.76	98.5	1.5
	0.2	10	0.85	98.8	1.2

*Volume precipitate is calculated as the percent volume of solid per cm³ reaction solution, assuming the precipitate is 100% vaterite (density = 2.54 g/cm³), rather than a mixture of calcite and vaterite. This assumption results in an overestimate of precipitate volume of up to 6%.

**Production of a viscous colloid prohibited measurement of precipitate mineralogy.

Carbonate source solutions were prepared individually and directly prior to each experiment to reduce the amount of CO₂ lost by equilibration and exsolution. Measured volumes of crystalline Na₂CO₃ or NaHCO₃ were added to Milli-Q water in a glass jar to produce final reactant solution concentrations ranging from 0.01 to 0.3 *M* (see Table 1). Source solutions were tightly capped with a threaded septum lid to avoid equilibration with the atmosphere, and the jar was agitated until all reagents dissolved. Upon complete dissolution, the carbonate source solution was withdrawn through the septum with a Hamilton gastight glass syringe. Reactants were immediately injected through gas-tight septa into the nitrogen-flushed Erlenmeyer vessel holding the calcium source solution. The reaction solution was stirred at 6000 rpm for the duration of the experiment using a magnetic stir bar and the pH of the reaction solution was monitored throughout the experimental procedure using a Denver Instrument Ultrabasic Benchtop pH meter. The stirring rate, which has been shown not to effect mineralogy or morphology of crystals in other vaterite precipitation experiments (Nancollas and Reddy, 1971; Weichers et al., 1975), assured a well-mixed solution in which the precipitate remained in suspension, allowing for representative aliquot sampling.

In most cases, precipitation occurred immediately upon injection of the carbonate solution and was evident by clouding of the solution. Aliquots of 10 to 30 mL were taken at five minutes intervals, beginning at less than one minute, with sterile syringes injected through gas-tight septa. The reaction was terminated at 10 to 25 minutes by filtering, drying, and weighing of the remaining sample. Each aliquot was vacuum-filtered through 0.45 µm Millipore membranes and the precipitate dried

at 120°C for 20 minutes. Dried precipitate was weighed and reserved for morphological analysis and identification of mineralogy. Previous work by Kralj et al. (1998) suggested that transformation of vaterite to a stable calcite phase is a solution mediated processes. Immediate filtering and rapid drying of samples, therefore, should inhibit transformation from vaterite to calcite.

A second set of experiments was undertaken to explore the incorporation of specific cations into rapidly precipitated vaterite precipitation (see Part II), one of which is described here. For these experiments, Mg^{2+} was added to solutions of 0.2 *M* CaCl_2 in concentrations equal to 1, 2, and 5 times present seawater concentration (53.2 *mM*; Millero and Sohn, 1992) and reacted with 0.2 *M* Na_2CO_3 or NaHCO_3 solutions. The desired Mg^{2+} concentrations were obtained by addition Mg^{2+} ICP standards (10,000 mg/L in 5% HNO_3). The addition of HNO_3 caused a decrease in solution pH and required titration to pH ~7 using 2.5 N NaOH prior to addition of carbonate source solutions. In these experiments, reactions were allowed to run for 5 minutes until terminated by filtration.

2.2. Morphological and mineralogical analysis

Morphology and crystal size of samples was confirmed by a combination of petrographic and scanning electron microscopy at the University of West Georgia using an FEI Quanta 200 environmental scanning electron microscope and at the University of Tennessee using a JEOL JSM6060 low vacuum scanning electron microscope.

Precipitate mineralogy was analyzed by X-ray diffraction (XRD) at the University of Tennessee using two diffractometers: 1) a Siemens D500 powder X-ray diffractometer with a $\text{CuK}\alpha$ X-ray tube, run at 40 kV and 30mA, at 0.02° increments with a dwell time of 4 seconds, over an angular range of $23-34^\circ 2\theta$ and 2) an INEL curved position-sensitive detector (PSD) with an output of 4096 channels (each $0.03^\circ 2\theta$ wide), using $\text{CuK}\alpha 1$ radiation, which was produced using a Ge111 monochromator, run at 20kV and 55mA. Percentages of vaterite and calcite were determined using a Jade XRD software semi-quantitative procedure, with relative intensity ratios of 1.2 and 3.0 for vaterite and calcite, respectively, as calculated by Materials Data Inc. using known crystal structures. Multiple sample analyses provided percentages $\pm 3\%$.

2.3. Volumetric determination

For each experiment, solution volumes were recorded and precipitates were filtered, dried, and weighed. Precipitate volume was determined using the density of vaterite (2.54 g/cm^3) and calculated as percent abundance of total reaction solution volume (150 to 250 cm^3 , depending on experiment). The assumption that the precipitate consisted of pure vaterite, rather than a mixture of vaterite and calcite (2.71 g/cm^3), results in an overestimation of precipitate volume of up to 6%.

3. Results

3.1. Reaction behavior

In each experiment, the addition of the carbonate source solution caused an immediate shift in solution pH, the extent of which increased with increasing reactant concentration. In experiments using equimolar, 0.2 M calcium and carbonate source solutions, the addition of the NaHCO₃ solutions resulted in a decrease in pH from initial values of pH = 7 to approximately pH = 6.8; by contrast, the addition of Na₂CO₃ solutions resulted in an increase in pH to approximately 9.9. Carbonate precipitation, as indicated by clouding of the solution, occurred concurrently with this pH shift.

When Na₂CO₃ was used as the carbonate source, most aliquots taken immediately upon mixing of the reactants were gelatinous in their consistency. Similar gelatinous material in experiments by Sawada et al. (1990) and Andreassen (2005) have been shown to consist of amorphous calcium carbonate (ACC). Reactions in which NaHCO₃ was used as the carbonate source did not produce this gelatinous substance. In most reactions, a rapid drop in solution pH of approximately 1 pH unit occurred between minutes two and three and was associated with dissipation of the gelatinous consistency, after which reaction solutions behaved as individual particles in solution. Similar drops in pH in other experimental procedures have been interpreted to signal the transformation of the ACC to either calcite, vaterite, or a mixture of the two (Sawada et al., 1990; Andreassen, 2005).

Exceptions to this behavior occurred when Mg^{2+} was added to Na_2CO_3 carbonate source solution experiments. At all Mg^{2+} concentrations (1, 2, and 5 times modern seawater), reactions produced a viscous colloid that were not associated with a rapid change in pH value or change in product consistency. When held at room temperature for 24 hours, the reaction product in the lowest Mg^{2+} experiment maintained the consistency of a viscous colloid; at higher concentrations, however, the colloid converted into a discrete liquid and precipitate phase. Aliquots of all concentrations reverted to liquid when placed into the oven and a formed a new precipitate of significantly smaller volume compared with initial colloid volume.

3.2. Precipitate morphology and size

SEM photomicrographs (Figures 7 and 8) show the range of morphology generated in precipitation reactions. Reactions of NaHCO_3 and Na_2CO_3 with 0.2 M Ca^{2+} source solutions produced primarily a spheroidal crystal morphology, ranging from 3 – 10 μm in diameter, during initial precipitation. Spheroidal morphologies were preserved throughout the reaction time with only minor increase in rhombic morphologies. Experiments with NaHCO_3 as a carbonate source showed a greater degree of recrystallization to rhombic form as the reaction progressed.

Figure 8 shows the variation in precipitate morphology produced in reactions with and without added trace elements. Reactions without added trace elements (Figures 8a,b) consist primarily of spheroidal crystals, with only minor rhombic and non-spheroidal morphologies. Precipitation in 0.2 M reactants in the presence of Fe^{2+} cations typically produced larger, more polygonal crystal morphologies (Figure

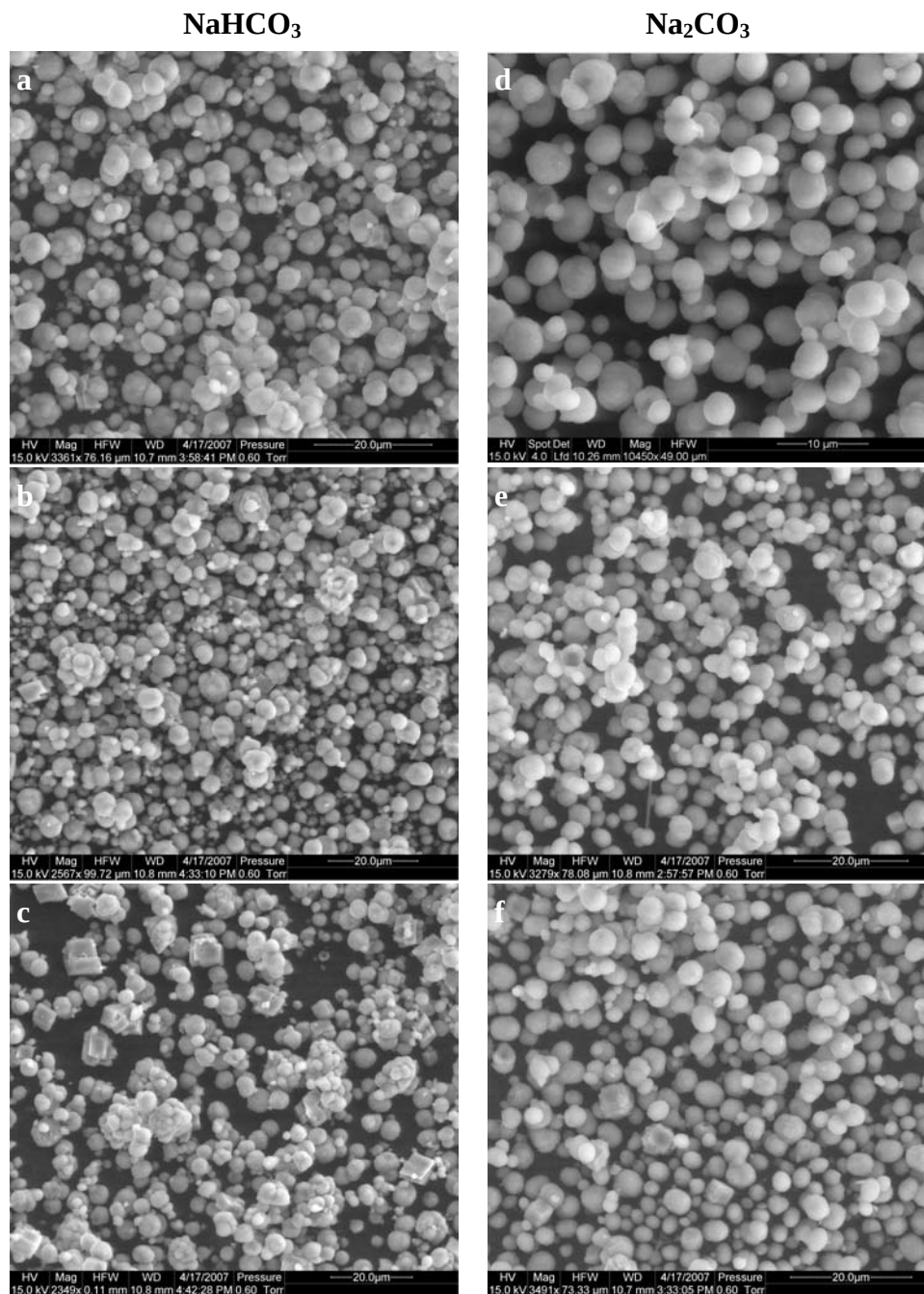


Figure 6. SEM images showing changes in precipitate morphology through time. (a-c) Rapidly precipitated calcite and vaterite produced in NaHCO₃ reaction solutions at 5 (a), 10 (b), and 15 (c) minutes show retention of spheroidal form in majority of crystals with some transformation to rhombic morphologies with time. (d-f) Rapidly precipitated calcite and vaterite produced in Na₂CO₃ reaction solutions at 10 (d), 15 (e), and 20 (f) minutes show retention of spheroidal form through time.

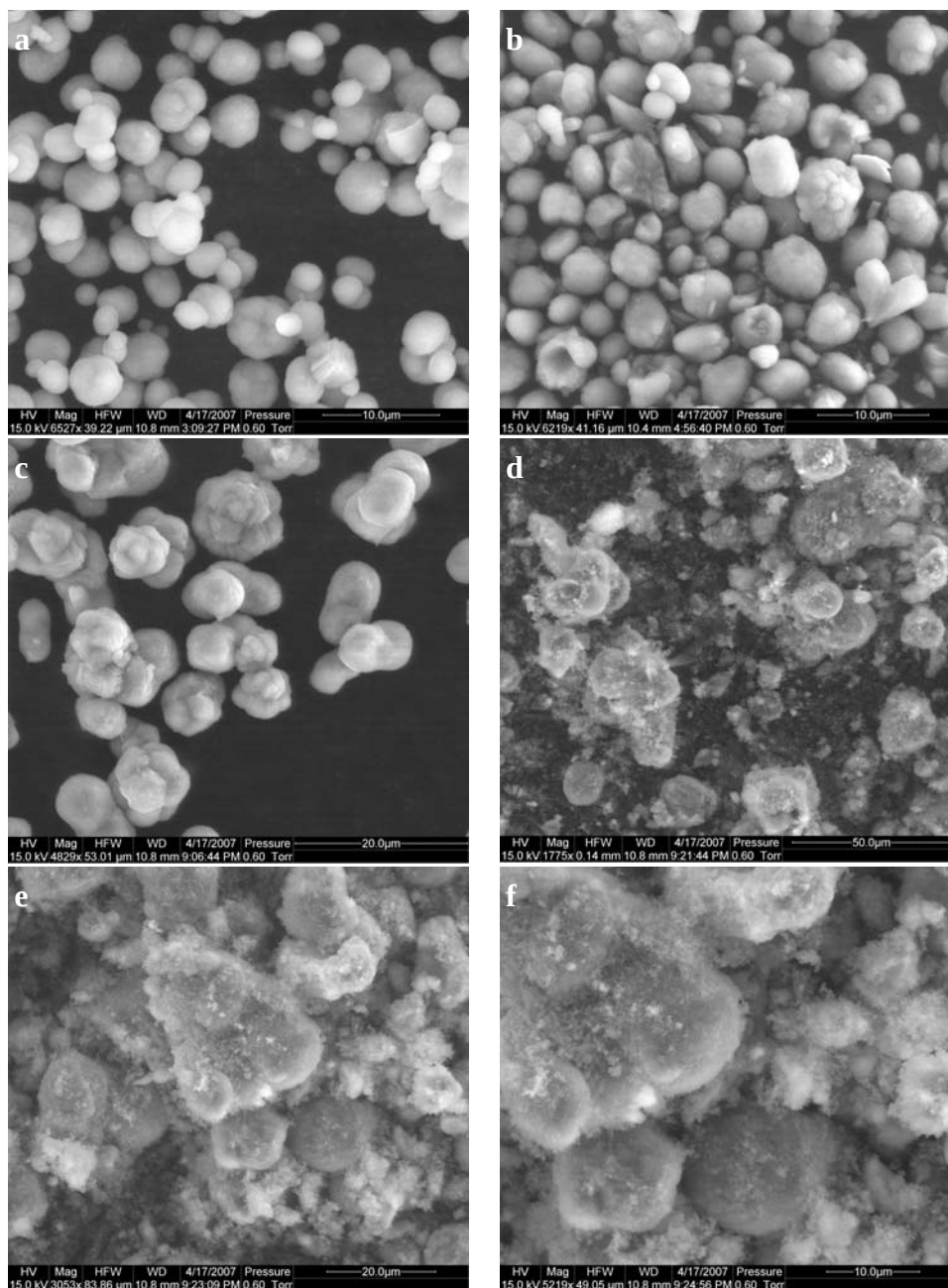


Figure 7. SEM photomicrographs showing variation in crystal morphology. (a) Spheroidal morphologies produced in $0.2\text{ M Na}_2\text{CO}_3$ reaction solutions at 5 minutes. (b) Sub-spheroidal and teardrop shaped crystals produced at 1 minute in 0.2 M NaHCO_3 reaction solutions. (c) Crystals produced at 5 minutes in Na_2CO_3 reaction solutions with added Fe^{2+} show more angular rosette morphologies. (d-f) Rounded crystals of irregular sizes and shapes produced in Na_2CO_3 reactions with added Mg^{2+} .

8c). Dried colloid from experiments with added Mg^{2+} show irregular spheroidal morphologies as well as abundant small, angular morphologies.

3.3. Precipitate mineralogy

Mineral percentages for precipitates as determined by XRD are reported in Table 1. Experimental procedures resulted in precipitate that varied from 0 to 98.8% vaterite. Additional minerals included calcite (up to 100%) and minor amounts of halite and one or more unidentified phases. Notably, experiments that used CaCl_2 and either Na_2CO_3 or NaHCO_3 carbonate source solutions in otherwise pure Milli-Q water were most successful in forming vaterite (see also Kralj et al., 1997; Sawada et al., 1990, Andreassen and Hounslow, 2004; Andreassen, 2005). In these cases, a mixture of calcite and vaterite formed, with vaterite ranging from 51.2 to 85.2% when Na_2CO_3 was used as the carbonate source, and from 86.9 to 95.8% when NaHCO_3 was used as the carbonate source. Experiments in which Milli-Q water was adjusted with NaCl to an initial ionic strength equal to seawater ($I = 0.7$) also resulted in precipitation of a mixture of calcite and vaterite. At reactant concentrations $< 0.2\text{ M}$, resulting precipitate was 12.8 to 59.3% vaterite. At reactant concentrations $\geq 0.2\text{ M}$, a combination of vaterite, calcite, and halite was produced. In each of these cases, the greatest percent of vaterite was produced at reactant concentrations of 0.2 M , and reactants using NaHCO_3 as the carbonate source consistently produced a greater percent of vaterite (Figure 8). Additionally, the largest percent of vaterite was

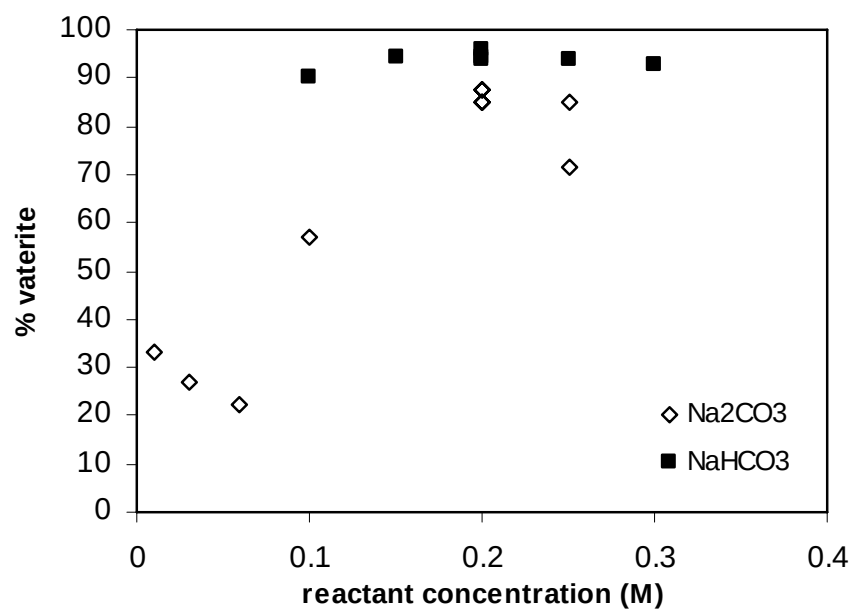


Figure 8. XRD analyses of the precipitate formed during reactions, in which Na₂CO₃ was used as the carbonate source, show an increase in percent vaterite produced with increasing reactant concentration. Although experiments in which NaHCO₃ was used as the carbonate source do not show increasing percent vaterite with increasing reactant concentration, these reactions produced a greater overall percent vaterite in comparison with Na₂CO₃ experiments.

identified in aliquots removed at 5 minutes and the percent vaterite precipitated decreased as the reactions progressed (Figure 9).

In contrast to experiments performed in pure Milli-Q water or Milli-Q water adjusted with NaCl to seawater ionic strength, experiments performed in synthetic seawater produced only calcite. Exceptions to this were experiments in which calcium acetate was used as the Ca^{2+} source. In both Milli-Q water and synthetic seawater solutions, addition of calcium acetate resulted in formation of a mixed calcite and vaterite precipitate. In Milli-Q water, vaterite varied from 43.2 to 96.7% of the total precipitate when Na_2CO_3 was used as the carbonate source, and between 97.5 and 98.9% when NaHCO_3 was used as the carbonate source. In synthetic seawater, addition of calcium acetate resulted in 7.1 to 72.3% vaterite when Na_2CO_3 was used as the carbonate source, and 10.1 to 97.6% when NaHCO_3 was used as the carbonate source, with vaterite percent increasing sharply with increasing reactant concentration (Figure 10).

3.4. Precipitate volume

Preprecipitate volumes are reported as percent of total aliquot volume for comparison with the observed 30% of MT structure filled by cores. All NaHCO_3 experiments produced significantly less precipitate than did Na_2CO_3 experiments (Figure 11). Maximum volume of precipitate formed in NaHCO_3 solutions was 1.24% and the maximum volume of precipitate formed in Na_2CO_3 was 2.75%. The maximum volume of precipitate produced in calcium acetate and Na_2CO_3

experiments was 2.75%. Calcium acetate and NaHCO_3 and experiments produced a maximum volume of 0.8%.

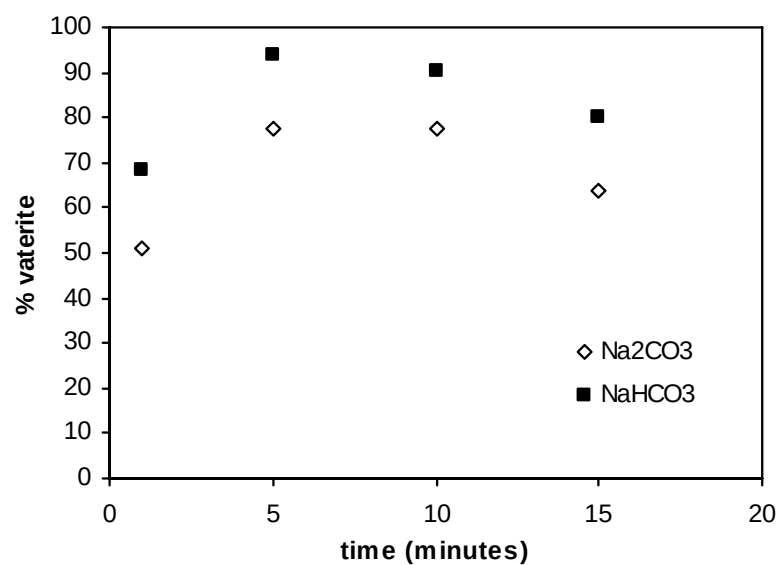


Figure 9. In experiments using 0.2 *M* reactant solutions in Milli-Q water, the greatest percent of vaterite was produced at *t* = 5 minutes. All of these experiments produced a binary mixture of calcite and vaterite and showed an increase in percent calcite as reactions progressed.

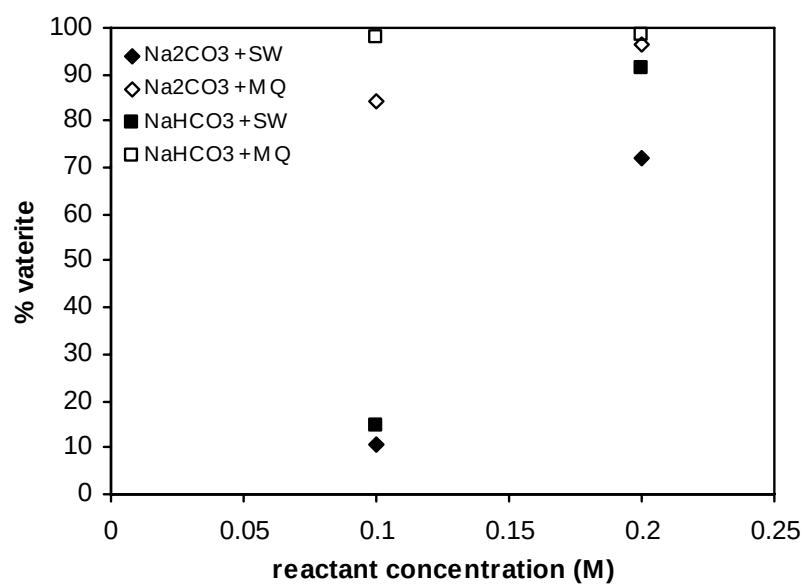


Figure 10. Percent vaterite produced in experiments using calcium acetate as the Ca^{2+} source. Reactions in which Milli-Q water (MQ) was used as the solute produced more vaterite than those performed in synthetic seawater (SW).

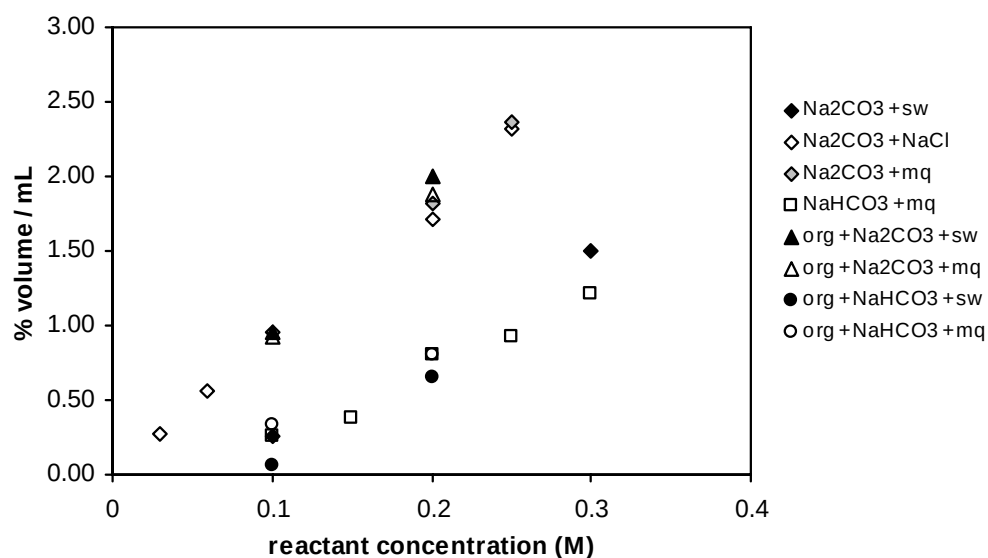


Figure 11. Percent volume of precipitate per mL solution for experiments run at a range of reactant concentrations (SW = synthetic seawater solute; NaCl = solute with ionic strength adjusted to 7 using NaCl; MQ = Milli-Q water solute; org = calcium acetate used for Ca²⁺ source). The largest amount of precipitate was produced in inorganic experiments using Na₂CO₃ as the carbonate source in Milli-Q water

4. Discussion

4.1. Vaterite as a mineralogical precursor to molar-tooth microspar

Vaterite has been proposed as a possible mineralogical precursor to MT microspar because of the similarity in size and morphology of experimentally precipitated vaterite and MT microspar cores (Gellatly and Winston, 1999; Crawford and Kah, 2004; Crawford, 2006; Pollock et al., 2006). Furthermore, petrographic and mineralogical analysis of MT microspar cores indicates that spheroidal cores likely underwent various degrees of recrystallization prior to precipitation of polygonal rim cements, suggesting a potentially metastable initial phase (Crawford, 2006). Similarly rapid recrystallization has been observed in vaterite precipitation experiments (Kralj et al. 1994, 1997, Abdel- Aal and Sawada, 2003; this study).

The size of carbonate crystals precipitated in this study is consistent with core sizes observed in geologic examples of MT microspar. Spheroidal MT microspar cores typically range from 5-8 μm in diameter (Crawford and Kah, 2004; Crawford, 2006; Pollock et al., 2006; Bishop et al., 2006a,b) and similar crystal sizes were consistently produced in these experiments (c.f. Figures 8a, b). In addition, although crystal morphologies exhibited by the experimentally produced precipitate were variable, they were dominantly spheroidal with minor rhombs. This, too, is consistent with observations of MT microspar. The mixture of morphologies observed here suggests that mixed spheroidal and rhombic crystals may be a primary feature of the precipitating phases and not necessarily a result of early diagenetic crystallization of spheroidal forms. Examples that show indication of recrystallization (e.g. zoned crystals; Figure 4b) probably represent early diagenetic alteration.

This study and others have shown that spheroidal crystals are not uniquely a phenomenon of vaterite precipitation. Spheroidal calcite has been shown to occur in the presence of certain microbial communities (Brehm et al., 2006), in gels doped with divalent cations (Fernandez-Diaz et al., 2006), in the presence of organic molecules (Du et al., 2005), and in highly saturated synthetic seawater solutions (this study). Therefore, the assumption cannot be made that all spheroidal crystals produced in these reactions consist solely of vaterite and that various euhedral morphologies represent a transitional phase between vaterite and more stable phases. It is possible, then, that the observed spheroidal nature of MT microspar cores may be attributed to the influence of supersaturated conditions, foreign cations, biological activity, or organic molecules, rather than to an originally vaterite mineralogy. These experiments also present the likely alternative that MT microspar may have formed as a polymineralic mixture of predominantly spheroidal CaCO_3 polymorphs, rather than as a single mineral phase.

Observed combinations of spheroidal and rhombic crystals produced in these experiments invite comparison with the model proposed by Crawford (2006) in which crystals nucleate spontaneously, grow by Ostwald ripening, and variable transformation to calcite before being cemented by rigid overgrowths. This study and others have shown that vaterite is an inherently unstable mineral phase in solution (Kralj et al., 1997) and the process of transformation may be similar to that proposed by Crawford (2006), although no mechanism for overgrowth precipitation (and therefore cessation of transformation) was explored in this study. It has been shown however, that a vaterite phase can be stabilized in the presence of templating organic

molecules (Hall and Taylor, 1978; Naka and Chujo 2001; Abdel-Aal and Sawada, 2003; Han et al, 2006). It is possible that the transformation from spheroidal morphologies to rhombic forms was inhibited by the presence of organic molecules in the Precambrian water column, allowing time for precipitation of overgrowth cements to form.

4.2. Precipitate volume constraints on molar-tooth microspar formation

The sedimentological character of molar-tooth structures requires rapid precipitation within newly formed voids to prevent void collapse. Pratt (1998) proposed a model for formation by which tectonic activity opened MT cracks and simultaneously filled them by injection of lime mud, which then diagenetically recrystallized to form MT microspar. Whereas this model addresses both the rapid infilling necessary to preserve MT structures as well as the volume of fill needed, petrographic analysis of MT microspar suggests that the lime mud injection model is not valid (Crawford, 2006; Bishop et al., 2006b). Although relatively few studies have focused on the origins of the microspar itself, those that have attribute MT microspar core crystallization to an initial CaCO_3 mineral phase, namely ACC (Bishop et al., 2006b), aragonite (Fairchild and Spiro, 1987), high-Mg calcite (Pratt, 1998), or vaterite (Gellatly and Winston, 1999; Crawford, 2006; Pollock, 2006), that precipitated from a void-filling solution and was subsequently cemented by growth of polygonal rims.

Any origin for MT microspar that assumes an initial carbonate phase must address the volume of cement needed to fill MT structures and the ionic strength of the fluids from which the precursor crystallized (cf. Bishop et al., 2006a). Simply,

assuming a precipitate density between that of calcite (2.71 g/cm^3) and vaterite (2.54 g/cm^3) and the molecular weight of CaCO_3 (100.089 g/mole), precipitation of 1 cm^3 CaCO_3 requires ~ 0.026 moles of Ca^{2+} . Assuming an average MT microspar crystal diameter of $12 \text{ }\mu\text{m}$ and core diameter of $8 \text{ }\mu\text{m}$, precipitation of cores alone requires ~ 0.008 moles of Ca^{2+} to fill 30% of 1 cm^3 of void space. Given the concentration of Ca in modern seawater (400 ppm or 0.01 M), this is 800x the molar Ca^{2+} concentration of modern seawater and 40x the molar Ca^{2+} concentration used in experiments performed here utilizing 0.2 M Ca^{2+} concentrations. At these concentrations, 0.8 L of modern seawater would be required to supply necessary Ca^{2+} ions for precipitation of 1 cm^3 MT cores. Precipitation yields in precipitation experiments were $< 30 \text{ mg precipitate per } 1 \text{ mL reaction solution}$, suggesting a maximum precipitation efficiency of 95%.

Because MT appears to form under non-evaporative, open marine conditions (James et al., 1998), Bishop et al. (2006a) invoked a wave-induced fluid flow model to address ion supply. In this scenario, wave loading during storm events would pump fluids through interconnected MT cracks, refreshing the ion supply to the system. However, several aspects make this model unlikely. First, it requires retention of void form even with active fluid pumping, yet Pollock et al. (2006) showed that cracks can be filled rapidly with collapse of unconsolidated matrix sand. The fluid pumping model also involves a continuous supply of ions and thus, continuous nucleation of new microspar cores, yet analysis of CSDs (Crawford, 2006) demands nucleation of microspar cores in a single nucleation event. Finally, this model does not adequately address petrographic evidence indicating that

microspar cores remained in suspension and did not come in contact with one another during precipitation of overgrowth cements. In experiments performed here, precipitate settled from suspension immediately upon cessation of stirring. It seems unlikely, therefore, that settling would not have occurred between periods of wave-induced flow.

Other considerations regarding ionic supply include the potential precipitation of polymineralic carbonate phases that incorporate both Ca^{2+} and Mg^{2+} in their crystal structures, as well as the potential for substantially higher concentration of cations in Precambrian marine waters. A divalent cation hypothesis takes into account ionic concentration of both Ca^{2+} (400 ppm or 0.012 M) and Mg^{2+} (1270 ppm or 0.053 M) in modern seawater and the potential for precipitation of a variety of mineral phases (calcite, aragonite, vaterite, hydrated calcitic and magnesian carbonates).

Calculations suggest that the increase in ionic strength provided by potential utilization of Mg^{2+} ions reduces the volume of fluid necessary to precipitate 1 cm³ of MT microspar to 0.5 L or 126 mL to precipitate initial cores.

We must also consider the potential for Precambrian seawater to have had very different ionic concentration. Precambrian pCO_2 and thus, DIC, are proposed to have been as high as 10x to 100x modern values (Grotzinger, 1990; Grotzinger and Kasting, 1993; Bartley and Kah, 2005). At these concentrations, a concomitant increase in alkalinity is required to maintain fluid pH capable of precipitating carbonate. This increase in alkalinity was likely controlled by increased carbonate dissolution on land and increased Ca^{2+} and Mg^{2+} delivery to the oceans. Petrographic (Tucker, 1982) and geochemical (Kah et al., 2001) evidence also suggest that despite

potentially higher Ca^{2+} concentrations (Grotzinger, 1989), Mg/Ca ratios of Precambrian seawater may also have been elevated over modern seawater ratios. Assuming DIC 10x modern values, and a concomitant 10-fold increase in divalent cation concentration of normal marine water ($\text{Ca}+\text{Mg} = 0.66 \text{ M}$), precipitation of $1 \text{ cm}^3 \text{ CaCO}_3$ would require only $\sim 12 \text{ mL}$ of fluid to supply the necessary cations. Such a scenario suggests that the abundance of MT microspar in the geologic record could be directly linked to pCO_2 and increased seawater alkalinity.

In addition to ionic supply, hypotheses regarding the origin of MT microspar must also satisfy the unique petrographic character of MT microspar. When observed in CL, MT cores exhibit luminescent properties distinct from overgrowth cements (Crawford, 2006; Pollock et al., 2006; Bishop et al., 2006b). Crawford (2006) also noted that MT microspar cores are depleted in Sr^{2+} and Mn^{2+} and enriched in Mg^{2+} , whereas polygonal rims are depleted in Mg^{2+} and enriched in Sr^{2+} and Mn^{2+} . Crawford (2006) and Bishop et al. (2006a,b) recognize three possibilities for the observed differences in core-overgrowth chemistry: 1) chemical exchange or refreshment of pore fluids, 2) a change in growth regime resulting in differential elemental incorporation, or 3) a change in precipitate mineralogy.

The compositional difference between core and overgrowth cements is unlikely to have resulted from introduction of chemically distinct fluids into MT structures. As discussed earlier, retention of void competence and the petrographic requirement that microspar cores remain in suspension throughout the cementation process precludes wholesale changes in fluid flow regime. Additionally, potentially recrystallized (i.e. rhombic, zoned) microspar cores are dispersed randomly

throughout MT structures (Crawford, 2006) rather than being concentrated at void walls or void centers, where fluid exchange is most likely to occur.

In a low flow model for microspar formation, it is possible, however, for compositional differences between core and overgrowth cements to result from differential incorporation trace elements associated with either: 1) a change in crystal growth rate, 2) a change in fluid chemistry with continued precipitation, or 3) a change in the precipitate mineralogy. Although slowing rates of precipitation during crystal growth is common in ion-limiting conditions (Kile et al., 2000), CSD analyses of Crawford (2006) suggest that only minor Ostwald ripening occurred prior to cessation of core growth. Overgrowth cements thus represent a distinctly different crystal growth phase. The change in chemistry of precipitating fluids and rate of ion delivery to sites of precipitation, however, can affect rates of carbonate precipitation, crystal morphology and mineralogy of precipitates, and trace element incorporation into the resulting precipitate (Gonzalez et al., 1992). Concentration of Mg^{2+} into rapidly precipitating carbonate phases is common (Sawada et al., 1990, this study Part II), so it is not surprising that cores are enriched in Mg^{2+} . Sr^{2+} , on the other hand, is most commonly enriched in aragonite phases (Holland et al., 1964), suggesting, perhaps, a mineralogical change.

4.3 Colloidal model for microspar precipitation

Fairchild et al. (1997), Pollock et al. (2006), and Bishop et al. (2006b) note, however, that within a single microspar crystal, cores and overgrowths are in optical continuity, even when two or more cores are encompassed by a single overgrowth; therefore overgrowth cements either grew 1) in lattice continuity with initial cores or

2) cores existed as amorphous CaCO_3 prior to cementation and later crystallized in optical continuity with external cement (Bishop et al., 2006b). In both of these scenarios, initial MT cores must remain in suspension during growth of sedimentary carbonate. For this to occur, fluid density must have been approximately equal to the density of the cores or ~ 2.5 to $2.7 \times$ the density of modern seawater. In the majority of precipitation experiments performed here, reaction fluid density did not equal that of the precipitate, as evidenced by rapid settling of crystals upon cessation of stirring. Experiments in high-alkalinity Na_2CO_3 solutions and those with added Mg^{2+} both formed a gelatinous, high-viscosity colloid upon initial precipitation. Previous experiments have suggested that this high viscosity stage is likely associated with formation of an initial amorphous, hydrated carbonate phase (Sawada et al., 1990; Andreassen, 2005).

Bishop et al. (2006b) propose a non-crystalline precursor to molar-tooth microspar to explain the optical continuity of MT microspar crystals despite chemical and perhaps original mineralogical differences between cores and rims. The increase in viscosity of Na_2CO_3 reaction fluids with added Mg^{2+} observed in this study may have important implications for the formation of Precambrian MT microspar because this substance could hold MT voids open during microspar crystallization, as well as be viscous enough to retain cores in suspension. These reactions show that under high carbonate saturation, a gel-like substance can be formed in the presence of low concentrations of exceedingly hydrated ions in fairly simple solutions.

Pore fluids in Precambrian ocean sediments may very well have had elevated DIC, divalent cations, and DOC derived from decomposition of organic matter.

Formation of a viscous colloid under these conditions would act to 1) keep initial precipitation in suspension with voids; 2) maintain integrity of void walls; and 3) act as a diffusion-limited barrier to ion transport that would potentially lead to very different growth rates of overgrowth cements, and associated differences in mineralogy and trace element incorporation. Furthermore, ACC is shown to precipitate as spheroidal masses in the presence of Mg^{2+} ; the presence of organic molecules may template and stabilize this morphology (Ajikumar et al., 2005).

5. Conclusion

- (1) Precipitation experiments presented here suggest that an initial MT microspar phase may have been a polymineralic mixture of vaterite, calcite, and possibly halite.
- (2) The observed range in crystal morphologies exhibited by the experimental precipitate are consistent with the MT microspar formation model for rapid nucleation followed by growth and transformation, proposed by Crawford (2006), although the mechanism for precipitation of overgrowth cements was not addressed by experimental studies.
- (3) If vaterite comprised a significant portion of MT microspar, its abundance may have resulted from the addition of organic molecules that acted to aid nucleation and stabilize spheroidal morphology.
- (4) Calculations of cation supply suggest that modern marine fluids are ion-limited in terms of precipitating the volumes of MT microspar observed in the geologic record. However, the combination of increased precipitation efficiency (via reduced inhibitors to crystallization or nucleation catalysts) and potentially elevated carbonate alkalinity could result in precipitation of volumes of crystals sufficient to fill and stabilize MT voids.
- (5) Triggering of an initially viscous colloid may provide the best mechanism of holding MT voids open during the lithification process. Although there is no clear mechanism for subsequent crystallization within the voids, it is possible that elevated concentrations of dissolved organic molecules, introduced in the migration of organically derived gas, could stabilize this substance.

**PART II: Trace element incorporation into experimentally
precipitated vaterite at 20°C**

Abstract

Calcium carbonate was precipitated from 0.2 M CaCl_2 and Na_2CO_3 or NaHCO_3 solutions at 20°C with the addition of various concentrations of trace elements (Mg^{2+} , Sr^{2+} , Mn^{2+} , and Fe^{2+}), to study the mode of incorporation of foreign ions and their effect on the mineralogy of rapidly precipitated carbonate phases. In most experiments, a binary precipitate of calcite and vaterite were produced, and the partition coefficients (D_{TE}) for incorporation of each trace element into vaterite determined by mass balance, using published D_{TE} values for calcite precipitated under similar conditions.

Experimental data show that incorporation of Mg^{2+} and Sr^{2+} into the precipitate increases with increasing concentration of these elements in reaction solutions; Mn^{2+} and Fe^{2+} showed the opposite trend. Experiments also showed the inhibiting effect of Mn^{2+} on vaterite formation on all CO_3^{2-} source solutions, and of Mg^{2+} and Fe^{2+} on vaterite formation in NaHCO_3 solutions. The opposite effect was observed in reaction solutions with added Sr^{2+} , which showed an increase percent in vaterite produced with increasing Sr^{2+} concentration.

1. Introduction

The vaterite-aragonite-calcite system is commonly studied because of the widespread precipitation of CaCO_3 minerals in nature, their importance in a variety of industrial applications, and the relative ease with which this system can be experimentally investigated, (Kralj and Brecevic, 1990; Clarkson et al., 1992; Kralj et al., 1997; Wolf et al., 2000; Dickenson et al., 2002; and others). Vaterite is the least stable polymorph of the vaterite-aragonite-calcite system. Vaterite commonly forms within highly saturated solutions where precipitation is most likely to be kinetically driven and strongly dependent on local conditions, such as temperature, saturation state, and the presence or absence of foreign ions (Clarkson et al., 1992). Vaterite precipitation is usually preceded by formation of a hydrated amorphous CaCO_3 (ACC) phase (Clarkson et al., 1992) and quickly transforms in solution to more thermodynamically stable calcite (Andreassen, 2004; Kralj et al., 1997). Crystal growth rates for vaterite have been estimated to be up to ten times higher than that of calcite (Andreassen, 2004; Kralj et al., 1997), and appreciable quantities of this metastable polymorph can be produced readily in solutions of high carbonate saturation. However, its kinetically controlled precipitation and metastable nature has inhibited understanding of the mechanisms of vaterite nucleation and growth, the influence of trace elements on vaterite crystallization and stability, and the incorporation of trace elements into vaterite mineralogy (Sawada et al., 1990; Clarkson et al., 1992; Dickenson et al., 2002).

Previous research on vaterite has focused on ameliorating its presence in industry, such as the prevention of vaterite scale in electrochemical water treatment

(Jaohari et al., 2000; Yang et al., 2000; Elfil and Hannachi, 2006). Vaterite is rarely associated with nonsedimentological processes but has been identified as a mineralogical curiosity in contact metamorphic terranes (McConnel, 1960; Kolodny and Gross, 1974) and as a mineralization product in gallstones (Bogren et al., 1995), urinary calculi (Prien and Frondel, 1947), and in the shells of chicken (Dennis et al., 1996) and gastropod (Hall and Taylor, 1971) eggs. Because most naturally formed vaterite is associated with either microbial processes, such as biomineralization in lacustrine (Giralt et al., 2001) and soil environments (Rodriguez-Navarro et al., 2007) or in extreme environments, such as supraglacial sulfur streams (Grasby, 2003) and cold water travertines (Lu et al., 2000), renewed interest in vaterite formation has focused largely on astrobiological studies and the potential use of vaterite as a mineralogical biomarker (Vecht and Ireland, 2000; Chekroun et al., 2004; Bosak and Newman, 2005).

Vaterite as a geologically important carbonate

Unfortunately, the rapid transformation of vaterite to calcite (Kralj and Brecevic, 1990; Clarkson et al., 1992; Kralj et al., 1997) has hindered the recognition of this metastable phase in the geologic record. Vaterite has, however, been proposed to be a potential mineralogical precursor to a petrographically distinct carbonate microspar (MT calcite of Furniss et al. 1998; Pollock et al. 2006; Bishop et al., 2006a,b). This unusual microspar, termed molar-tooth (MT) microspar, occurs almost exclusively in Mesoproterozoic and early Neoproterozoic shallow marine successions (James et al., 1998; Shields, 2002). Molar-tooth microspar typically occurs as uniform, equant, non-interlocking calcite crystals, averaging from 9-12 μm

in diameter (see Part I, Figure 1), that precipitates within molar-tooth structures (O’Conner 1972; Furniss et al., 1998; Pratt 1998) and more rarely at the sediment-water interface (Pollock, 2006, Bartley and Kah, 2007). Molar-tooth structures are a complex and interconnected network of spheroidal, spindle, and ribbon-shaped voids (see Part I, Figure 2) whose origin remains uncertain (O’Conner, 1972; Knoll and Swett, 1990; Fairchild et al., 1997; Pratt, 1998; Marshall and Anglin, 2004) but which may have resulted from the migration within unlithified sediments of gases derived from decomposing organic matter (Furniss et al., 1998; Pollock et al., 2006).

Initially Gellatly and Winston (1998) proposed vaterite as a potential mineralogical precursor to MT microspar based on uniformity of crystal size between MT microspar and simple vaterite precipitation experiments. Furthermore, sharp contacts between MT microspar and adjacent carbonate phases, non-interlocking grains, and the absence of petrographic inclusions suggest that MT microspar represents in situ precipitation (see Part I, Figure 3; Crawford, 2005; Pollock, 2006). Finally, cathodoluminescence (CL) analysis revealed MT microspar to be a two-phase precipitate, consisting of spheroidal to rhombic, dull-luminescent cores surrounded by more luminescent (i.e. Mn^{2+} -rich; Hemming et al., 1996), isopachous to polygonal rims (see Part 1, Figure 4; Fairchild, 1997; Crawford, 2005; Pollock et al., 2006; Bishop et al., 2006a,b). Largely spheroidal cores observed within MT microspar are consistent with morphologies of laboratory precipitated vaterite formed at highly elevated carbonate saturations and in the presence of a variety dissolved organic molecules (Kralj et al. 1994, 1997; Sawada et al. 1990; Naka and Chujo 2001; Chekroun et al., 2005; Du et al., 2005; Bosak and Newman, 2005).

Detailed petrographic and geochemical analyses of MT microspar collected from the United States, Canada, China, Russia, and Mauritania have supported interpretations of vaterite as a potential mineralogical precursor (Crawford, 2005). CL analyses of these geologic samples, which range in age from 1400 – 800 Ma, suggest that similar precipitation processes occurred in marine environments on a global scale. Analysis of crystal size distributions of microspar cores observed in CL indicate spontaneous nucleation and rapid crystal growth, followed by varying degrees of Ostwald ripening (Crawford, 2005; cf. Kile and Eberl, 2003). Such interpretation is consistent with rapid precipitation of spheroidal vaterite and subsequent transformation to rhombic calcite, as observed in laboratory experiments (Kralj et al., 1998; Sawada et al., 1990). Samples in which crystal size distributions suggest greater degrees of Ostwald ripening also show a higher proportion of zoned, rhombic cores, suggesting that recrystallization of cores occurred very rapidly, prior to precipitation of isopachous overgrowth cements. Although currently calcitic, MT microspar cores also show anomalous Raman spectral peaks that may reflect crystal structure defects associated with high trace element incorporation or mineralogical inversion from an unstable crystal form (Crawford, 2005).

The study of Crawford (2005) also noted, via SIMS ion imaging analysis, that MT microspar cores are depleted in Sr^{2+} and Mn^{2+} and enriched in Mg^{2+} relative to polygonal rims. Qualitative evaluation of Mg^{2+} enrichment observed in MT microspar cores suggest concentrations possibly exceeding that expected from a Mg-rich calcite phase, which is consistent with enrichments observed by Sawada et al. (1990) for experimentally precipitated vaterite. These lines of evidence, in addition to the

limited time frame over which this fabric is abundant (James et al., 1998), suggest that vaterite may have been an important component of Proterozoic marine environments. The work of Crawford (2005) suggests that trace element analysis may be an effective method of determining the occurrence of vaterite precipitation in the geologic record.

Trace element distribution in rapidly precipitated carbonate phases

The distribution of a trace element between a carbonate phase and solution is referred to as the partition coefficient (Morse and Bender, 1990). Under equilibrium conditions, the partition coefficient for a particular mineral phase can be modeled thermodynamically (Vaslow and Boyd, 1952; Hermann, 1961; McIntire, 1963, Sverjensky, 1984, 1985; Driessens, 1986). Experimentally determined partition coefficients, however, can deviate significantly from theoretical values (Rimstidt et al., 1998) because saturation state, temperature, and the behavior of chemical species in solution all effect precipitation rate (McIntire, 1963; Angus et al., 1979; Bunsenburg and Plummer, 1985; Pingatore and Eastman, 1986, Clarkson, 1992; Rimstidt et al., 1998; Teng et al., 2000; Watson, 2004). In particular, at high precipitation rates precipitation dynamics are typically dominated by kinetics, rather than by equilibrium, adsorption, occlusion, and increased numbers of lattice defects are likely to affect trace element incorporation (Bunsenburg and Plummer, 1985; Pingatore and Eastman, 1986). Because CaCO_3 minerals grow rapidly at relatively low temperatures, their trace element incorporation usually occurs by occlusion- the trapping of heterogeneous phases within the crystal structure (Rimstidt et al., 1998

McIntire, 1963; Bunsenburg and Plummer, 1985; Pingatore and Eastman, 1986; Teng et al., 2000; Watson, 2004).

Because vaterite is strongly influenced by kinetics during precipitation, is inherently unstable in aqueous solutions, and is relatively rare in nature, trace element incorporation into vaterite has not been studied extensively. Sawada et al. (1990) precipitated mixtures of calcite and vaterite at 25°C under conditions of high carbonate saturation and in the presence of Mg^{2+} . The results of that study showed that at very rapid precipitation rates, CaCO_3 polymorphs incorporate very high levels of Mg^{2+} into their crystal structures. In particular, vaterite incorporates up to 6.9x more Mg^{2+} into its mineralogy than does calcite precipitated under near-equilibrium conditions (Sawada et al., 2000).

This study explores the partitioning of Mg^{2+} , Sr^{2+} , Mn^{2+} and Fe^{2+} into vaterite. Each of these elements is commonly associated with either primary or diagenetic formation of sedimentary carbonates. Incorporation of trace elements into carbonate minerals is typically a rate dependent process (Rimstidt et al., 1998, Dromgoole and Walter, 1990; Morse and Bender 1990) and thus of limited use in interpreting the geologic record where rates can rarely be determined. Determination of trace element incorporation, however, may be more determinative when compared to geologic examples such as MT microspar that have been independently shown to result from rapid precipitation.

2. Methods

2.1. Experimental procedure

Reactions were carried out at room temperature (20°C) in a modified Erlenmeyer flask that allows for reagent input and aliquot withdrawal through rubber septa without opening the system to the ambient atmosphere (see Part I, Figure 5). All reactants used in the precipitation experiments were reagent grade. Reactant solutions, excluding Ricca brand synthetic seawater, were prepared using Millipore Milli-Q water.

For each experiment, a calcium source solution was added to the Erlenmeyer flask. Molar concentrations reported here represent the concentration of each species in the total reaction solution (see appendix for reactant concentrations prior to mixing). These solutions were made by mixing crystalline CaCl_2 in Milli-Q water. The flask was then flushed with nitrogen gas to remove atmospheric gases and capped with a rubber stopper fitted with a pH electrode.

Carbonate source solutions were prepared individually and directly prior to each experimental procedure, so as to reduce the amount of CO_2 lost by equilibration and exsolution. Measured volumes of crystalline Na_2CO_3 or NaHCO_3 were added to Milli-Q water to produce final reactant solution concentrations ranging from 0.01 to 0.3 M. Source solutions were tightly capped with a threaded septum lid to avoid equilibration with the atmosphere and the jar was agitated until all reagents had dissolved. Upon complete dissolution, the carbonate source solution was withdrawn through the septum with a Hamilton gastight glass syringe. Reactants were then immediately injected through gas-tight septa, into the nitrogen-flushed Erlenmeyer

vessel holding the calcium source solution. The reaction solution was stirred at 6000 rpm for the duration of the experiment using a magnetic stir bar and the pH of the reaction solution was monitored throughout the experimental procedure using a Denver Instrument Ultrabasic Benchtop pH meter. The stirring rate, which has been shown not to effect mineralogy and morphology of crystals in other vaterite precipitation experiments (Nancollas and Reddy, 1971; Weichers et al., 1975), assured a well-mixed solution in which the precipitate remained in suspension, allowing for representative aliquot sampling.

2.2. Addition of trace elements

Distribution of trace elements into vaterite was examined for four elements (Mg^{2+} , Sr^{2+} , Mn^{2+} , and Fe^{2+}) at three concentrations each in reaction solutions of 0.2 M CaCl_2 and Na_2CO_3 or NaHCO_3 (Tables 2 and 3). Mg^{2+} incorporation was examined at present seawater concentration (53.2 mM; Millero and Sohn, 1992), and two and five times present seawater concentration. Sr^{2+} incorporation was examined at present seawater concentration (90 μM ; Millero and Sohn, 1992), and two and ten times present seawater concentration. Mn^{2+} and Fe^{2+} were examined at trace cation to Ca^{2+} ratios of 0.001, 0.1, and 0.2, following calcite precipitation experiments of Dromgoole and Walter (1990). A stock solution of CaCl_2 and trace element was mixed for each set of concentrations to produce total reactant solution concentrations of 0.2 M CaCl_2 and desired concentration of trace element. These were used within 5 hours to prevent oxidation. Trace element concentrations were obtained by addition

Table 2. Trace element and Ca²⁺ reactant concentrations; precipitate mass, mineralogy, and chemistry; filtrate chemistry.

Trace element	Trace element reaction solution (ppm)	Ca ²⁺ reaction solution (ppm)	precip. mass (mg/mL)	% vaterite	% calcite	Mn ²⁺ ppm	Fe ²⁺ ppm	Mg ²⁺ ppm	Ca ²⁺ ppm	Sr ²⁺ ppm*	Mn ²⁺ ppm	Fe ²⁺ ppm	Mg ²⁺ ppm	Ca ²⁺ ppm	Sr ²⁺ ppm*
Na ₂ CO ₃ reactions						Solid (ppm)					Filtrate (ppm)				
Mg ²⁺															
Mg-c-Pc(1)	1309.77	8016	unknown	0	n/a**	0.0	0.0	813.0	678.0	0.3	0.0	0.0	10.9	271.2	0.0
Mg-c-2xc(1)	2619.54	8016	unknown	0	n/a**	0.0	0.0	1840.9	1121.7	0.6	0.0	0.0	9.1	113.9	0.0
Mg-c-5x(1)	2752.73	8016	unknown	0	n/a**	0.0	0.0	4344.0	1951.0	1.5	0.0	0.0	66.1	312.2	0.1
Sr ²⁺															
Sr-c-Pc(1)	7.87	8016	1.356	59.9	40.1	0.0	0.0	0.5	219.6	0.3	0.0	0.0	0.0	14.0	0.3
Sr-c-2xc(1)	15.80	8016	1.37	72.1	27.9	0.0	0.0	0.0	270.9	0.5	0.0	0.0	0.0	169.0	3.1
Sr-c-2xc(2)	15.80	8016	1.37	69.5	30.5	0.0	0.0	0.0	235.7	0.4	0.0	0.0	0.0	206.0	2.4
Sr-c-10xc(1)	78.88	8016	1.388	78.6	21.4	0.0	0.0	0.0	76.1	0.6	0.2	1.0	0.0	140.0	9.9
Fe ²⁺															
Fe-c-001(1)	5.61	8016	2.843	64.4	35.6	0.0	0.5	0.5	732.2	0.1	0.0	0.0	0.0	105.0	0.2
Fe-c-001(2)	5.61	8016	2.842	65.8	34.2	0.0	0.7	0.4	900.8	0.1	0.2	0.0	0.0	176.0	0.4
Fe-c-01(1)	1128.79	8016	2.807	40.8	59.2	0.0	3.9	0.0	339.3	0.1	0.2	3.0	0.0	190.0	0.4
Fe-c-01(2)	1128.79	8016	2.736	83.9	16.1	0.0	3.7	0.0	325.7	0.1	0.0	0.6	0.0	261.0	0.4
Mn ²⁺															
Mn-c-001c(1)	3.51	8016	2.775	82.3	17.7	0.7	0.0	0.0	347.4	0.1	0.0	0.0	0.0	77.0	0.2
Mn-c-001c(2)	3.51	8016	2.822	80	20	0.8	0.1	0.4	373.1	0.1	0.2	0.0	0.0	100.0	0.4
Mn-c-01c(1)	70.72	8016	2.78	26.2	73.8	1.8	0.0	0.0	135.5	0.0	0.2	0.8	0.0	245.0	0.3
Mn-c-01c(2)	70.72	8016	2.851	31.1	68.9	2.6	0.0	0.0	184.9	0.0	0.1	0.1	0.0	139.0	0.2
Mn-c-05c(1)	351.29	8016	2.842	0	n/a**	1.6	0.0	0.0	23.6	0.0	1.9	0.0	0.0	454.0	0.3
Mn-c-05c(2)	351.29	8016	2.891	14.6	85.4	2.3	0.0	0.0	33.8	0.0	4.2	0.1	0.0	484.0	0.3

Table 2. Continued.

Trace element	Trace element reaction solution (ppm)	Ca ²⁺ reaction solution (ppm)	precip. Mass (mg/mL)	% vaterite	% calcite	Mn ²⁺ ppm	Fe ²⁺ ppm	Mg ²⁺ ppm	Ca ²⁺ ppm	Sr ²⁺ ppm*	Mn ²⁺ ppm	Fe ²⁺ ppm	Mg ²⁺ ppm	Ca ²⁺ ppm	Sr ²⁺ ppm*
NaHCO ₃ reactions						Solid (ppm)					Filtrate (ppm)				
Mg ²⁺															
Mg-bc-P(1)	2752.73	8016	0.789	86.3	13.7	0.0	0.0	4.0	856.9	0.1	0.0	0.0	1541.5	4900.4	1.7
Mg-bc-P(2)	1316.52	8016	0.787	84.8	15.2	0.0	0.0	3.0	1005.1	0.1	0.0	0.0	1297.7	5741.5	1.7
Mg-bc-2x(2)	2616.16	8016	0.404	66.7	33.3	0.0	0.0	5.3	625.4	0.1	0.0	0.0	2592.3	4166.2	1.8
Mg-bc-2x(1)	2616.16	8016	0.35	67.5	32.5	0.0	0.0	7.2	557.1	0.1	0.0	0.0	2480.9	4052.8	1.7
Mg-bc-5x(2)	5445.51	8016	0.204	78.2	21.8	0.0	0.0	8.6	256.3	0.1	0.0	0.0	4242.7	5419.6	3.2
Mg-bc-5x(1)	3683.73	8016	0.178	0	100	0.0	0.0	10.3	332.2	0.1	0.0	0.0	5058.7	6248.7	3.2
Sr ²⁺															
Sr-bc-P(1)	4.54	8016	1.068	76.3	23.7	0.0	0.0	0.0	859.8	0.3	0.0	0.0	0.0	4608.7	7.4
Sr-bc-P(2)	7.89	8016	1.056	79.8	20.2	0.0	0.0	0.0	936.5	0.3	0.0	0.0	0.0	4914.3	6.5
Sr-bc-2x(1)	15.77	8016	0.975	75.8	24.2	0.0	0.0	0.0	544.5	0.3	0.0	0.0	0.0	18049.4	39.3
Sr-bc-2x(2)	15.77	8016	0.837	83.5	16.5	0.0	0.0	0.0	1085.0	0.5	0.0	0.0	0.0	20344.7	41.2
Sr-bc-10x(1)	78.88	8016	0.817	93.6	6.4	0.0	0.0	0.0	347.3	0.9	0.0	0.0	0.0	965.3	12.0
Sr-bc-10x(2)	78.88	8016	0.835	85.4	14.6	0.0	0.0	0.0	506.4	1.3	0.0	0.0	0.0	184620	1662.6

Table 2. Continued.

Trace element	Trace element reaction solution (ppm)	Ca ²⁺ reaction solution (ppm)	precip. mass (mg/mL)	% vaterite	% calcite	Mn ²⁺ ppm	Fe ²⁺ ppm	Mg ²⁺ ppm	Ca ²⁺ ppm	Sr ²⁺ ppm*	Mn ²⁺ ppm	Fe ²⁺ ppm	Mg ²⁺ ppm	Ca ²⁺ ppm	Sr ²⁺ ppm*
NaHCO ₃ reactions						Solid (ppm)					Filtrate (ppm)				
Fe ²⁺															
Fe-bc-001(1)	5.61	8016	1.011	90.4	9.6	0.0	1.1	0.4	674.8	0.0	0.0	1.3	0.0	4680.0	1.4
Fe-bc-001(2)	5.61	8016	0.997	83.8	16.2	0.0	2.0	0.3	1136.6	0.1	0.0	1.3	0.0	5162.4	1.4
Fe-bc-01(1)	560.63	8016	0.746	0	100	0.0	2.9	0.0	156.8	0.0	0.0	17.6	0.0	4563.0	1.2
Fe-bc-01(2)	560.63	8016	0.798	0	100	0.0	2.3	0.5	137.3	0.0	0.0	62.1	0.0	4712.2	1.2
Fe-bc-05(1)	1128.79	8016	0.535	0	n/a**	0.0	11.0	0.0	55.1	0.0	0.3	60.2	0.0	3681.1	0.9
Fe-bc-05(2)	1128.79	8016	0.564	0	n/a**	0.0	14.4	0.0	71.0	0.0	0.0	5.0	0.0	3152.4	0.8
Mn ²⁺															
Mn-bc-001c(1)	2.38	8016	1.023	87.7	12.3	2.2	0.1	0.4	533.8	0.0	1.0	0.1	0.0	4307.3	1.4
Mn-bc-001c(2)	3.51	8016	0.965	90.1	9.9	1.1	0.0	0.4	241.4	0.0	1.6	0.1	0.0	4917.7	1.5
Mn-bc-01c(1)	70.72	8016	0.84	0	n/a**	2.4	0.1	0.0	90.1	0.0	24.1	0.0	0.0	4590.0	1.3
Mn-bc-01c(2)	70.72	8016	0.963	0	n/a**	2.1	0.0	0.0	71.7	0.0	18.0	0.2	0.0	4744.0	1.4
Mn-bc-05c(1)	351.29	8016	1.073	0	n/a**	2.1	0.0	0.0	15.0	0.0	114.0	2.3	0.0	5113.2	1.3
Mn-bc-05c(2)	351.29	8016	0.853	0	n/a**	2.7	0.0	0.0	18.3	0.0	130.7	0.0	0.0	5284.6	1.6

*Small and consistent concentrations of Sr²⁺ in all experiments indicated Sr²⁺ contamination in Na₂CO₃ and NaHCO₃ powders; this amount was subtracted from concentrations in Sr²⁺ doped experiments.

**Unidentified phase

Table 3. Trace element reaction concentrations and calculated partition coefficients.

Trace element	m_{TE}	$m_{TE}/m_{Ca^{2+}}$	$*D_{calcite}$	$**D_{calcite}$ range	D_{total}	$D_{vaterite}$
<i>Na₂CO₃ reactions</i>						
Mg²⁺	0.0532	0.266	-	0.012 - 0.071 (1)	0.059	-
	0.1064	0.532	-		0.081	-
	0.532	2.66	-		0.140	-
Sr²⁺	9.0×10^{-5}	4.5×10^{-4}	0.1 ^{††}	0.03 - 0.4 (2)	0.128	0.147
	1.8×10^{-4}	9.0×10^{-4}	0.1		0.274	0.334
	1.8×10^{-4}	9.0×10^{-4}	0.1		0.180	0.212
	9.0×10^{-4}	4.5×10^{-3}	0.1		0.176	0.209
	9.0×10^{-4}	4.5×10^{-3}	0.1		0.207	0.236
Fe²⁺	2.0×10^{-4}	0.001	3.7 ^{†††}	3.7 (3)	1.058	-0.402
	2.0×10^{-4}	0.001	3.7		1.051	-0.325
	0.002	0.01	3.7		0.765	-3.493
	0.002	0.01	3.7		1.392	0.949
	0.01	0.05	-		1.692	-
Mn²⁺	2.0×10^{-4}	0.001	15.8 ^{†††}	1 – 50 (4)	2.295	-0.609
	2.0×10^{-4}	0.001	15.8		1.302	-2.322
	0.002	0.01	15.8		1.816	-37.574
	0.002	0.01	15.8		1.902	-28.889
	0.01	0.05	-		1.856	-
	0.01	0.05	15.8		1.759	-80.368

* $D_{calcite}$ is the value chosen for mass balance equation to determine D_{TE} in this study.

** $D_{calcite}$ range is range of reported D_{TE} values for experimentally precipitated vaterite

(1) Mucci and Morse (1983), Mucci (1998), Katz (1973), Sawada et al. (1990)

(2) Kitano et al. (1971), Holland (1964), Katz (1973), Lorens (1981), Mucci and Morse (1983), Pingatore et al. (1986)

(3) Dromgoole and Walter (1990), Pingatore et al. (1988), Lorens (1981)

(4) Dromgoole and Walter (1990)

†† $D_{Sr^{2+}(calcite)}$ from Lorens (1981) was chosen for mass balance equation because of similar experimental conditions (low temperature, high precipitation rate).

††† $D_{Mn^{2+}(calcite)}$ and $D_{Fe^{2+}}$ from Dromgoole and Walter (1990) was chosen for mass balance equations because of similar trace element concentrations (same $m_{TE}/m_{Ca^{2+}}$)

Table 3. Continued.

Trace element	m_{TE}	$m_{TE}/m_{Ca^{2+}}$	$*D_{calcite}$	$**D_{calcite}$ range	D_{total}	$D_{vaterite}$
<i>NaHCO₃ reactions</i>						
Mg²⁺	0.0532	0.266	0.036 [†]	0.012 - 0.071 (1)	0.020	0.017
	0.0532	0.266	0.036		0.009	0.005
	0.1064	0.532	0.036		0.028	0.024
	0.1064	0.532	0.036		0.018	0.009
	0.532	2.66	0.036		0.038	0.039
	0.532	2.66	-		0.042	-
Sr²⁺	9.0×10^{-5}	4.5×10^{-4}	0.1 ^{††}	0.03 - 0.4 (2)	0.241	0.285
	9.0×10^{-5}	4.5×10^{-4}	0.1		0.266	0.308
	1.8×10^{-4}	9.0×10^{-4}	0.1		0.298	0.361
	1.8×10^{-4}	9.0×10^{-4}	0.1		0.238	0.265
	9.0×10^{-4}	4.5×10^{-3}	0.1		0.223	0.232
	9.0×10^{-4}	4.5×10^{-3}	0.1		0.273	0.302
Fe²⁺	2.0×10^{-4}	0.001	3.7 ^{†††}	3.7 (3)	1.999	1.818
	2.0×10^{-4}	0.001	3.7		2.134	1.831
	0.002	0.01	-		2.079	-
	0.002	0.01	-		1.241	-
	0.01	0.05	-		4.640	-
	0.01	0.05	-		5.695	-
Mn²⁺	2.0×10^{-4}	0.001	15.8 ^{†††}	1 - 50 (4)	5.268	3.791
	2.0×10^{-4}	0.001	15.8		5.226	4.064
	0.002	0.01	-		2.774	-
	0.002	0.01	-		3.389	-
	0.01	0.05	-		3.070	-
	0.01	0.05	-		3.192	-

* $D_{calcite}$ is the value chosen for mass balance equation to determine D_{TE} in this study.

** $D_{calcite}$ range is range of reported D_{TE} values for experimentally precipitated vaterite

(1) Mucci and Morse (1983), Mucci (1998), Katz (1973), Sawada et al. (1990)

(2) Kitano et al. (1971), Holland (1964), Katz (1973), Lorens (1981), Mucci and Morse (1983), Pingatore et al. (1986)

(3) Dromgoole and Walter (1990), Pingatore et al. (1988), Lorens (1981)

(4) Dromgoole and Walter (1990)

[†] $D_{Mg^{2+}}$ for calcite rapidly formed from transformation of ACC was chosen from Sawada et al. (1990) for mass balance equations because of similar experimental conditions (high precipitation rate).

^{††} $D_{Sr^{2+}(calcite)}$ from Lorens (1981) was chosen for mass balance equation because of similar experimental conditions (high precipitation rate).

^{†††} $D_{Mn^{2+}(calcite)}$ and $D_{Fe^{2+}}$ from Dromgoole and Walter (1990) was chosen for mass balance equations because of similar trace element concentrations (same $m_{TE}/m_{Ca^{2+}}$)

into the stock solution of Sr^{2+} and Mg^{2+} ICP standards (1000 mg/L Sr^{2+} and 10,000 mg/L Mg^{2+} in 5% HNO_3), or crystalline $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. The addition of HNO_3 along with Sr^{2+} and Mg^{2+} caused a decrease in solution pH which was then titrated to pH ~ 7 using 2.5 N NaOH.

In most cases, four experiments were performed for each trace element concentration: including replicate experiments using both Na_2CO_3 and NaHCO_3 carbonate source solutions. Carbonate source solutions were injected into the nitrogen-flushed vessel containing the trace element doped stock solution and reactions were allowed to run until terminated by filtration at 5 minutes. A portion of the precipitate was removed immediately for mineralogical analysis via XRD and the filtrate was reserved for elemental analysis. The remaining precipitate was rinsed with 10^{-3} M ethylenediamine tetramethalyne phosphonic acid (EDTMP), which has been suggested to inhibit vaterite-calcite transformation (Abdel-Aal and Sawada, 2003). Precipitate aliquots were then dried at 120°C for 20 minutes, weighed, and reserved for further analysis.

2.3. Mineralogical and chemical analysis

Precipitate mineralogy was analyzed by X-ray diffraction (XRD) at the University of Tennessee using two diffractometers: 1) a Siemens D500 powder X-ray diffractometer with a $\text{CuK}\alpha$ X-ray tube, run at 40 kV and 30mA, at 0.02° increments with a dwell time of 4 seconds, over an angular range of $23-34\ 2\theta$ and 2) an INEL curved position-sensitive detector (PSD) with an output of 4096 channels (each $0.03^\circ\ 2\theta$ wide), using $\text{CuK}\alpha 1$ radiation, which was produced using a Ge111

monochromator, run at 20kV and 55mA. Percentages of vaterite and calcite were determined using a Jade XRD software semi-quantitative procedure, with relative intensity ratios of 1.2 and 3.0 for vaterite and calcite, respectively, as calculated by Materials Data Inc., using known crystal structures (see Figure 6). Multiple sample analyses provided percentages $\pm 3\%$.

One to two grams of each sample powder was digested for 2 hours in trace metal grade 2% HNO₃ for elemental analysis. Elemental concentrations of the acidified precipitate and reserved filtrate were analyzed at the University of West Georgia using a Perkin-Elmer inductively coupled plasma atomic emission spectrometer (ICP-AES) fitted with a Meinhardt concentric nebulizer. Precision and reproducibility for all elements analyzed are better than 10%, based on replicate measurements of synthetic laboratory standards.

2.4. Simple seawater experiments

To determine the conditions under which the greatest ratio of vaterite to calcite would form, several initial experiments were performed using a variety of reactant concentrations without the addition of trace elements (see Part I; Table 1). In most cases, precipitation occurred immediately upon injection of the carbonate solution and was evident by clouding of the solution. Aliquots of 10 to 30 mL were taken at five minute intervals, beginning at less than one minute, with sterile syringes injected through gas-tight septa. Aliquots were vacuum filtered through 0.45 μm Millipore membranes and the precipitate was dried at 120°C for 20 minutes. The dried precipitate was then weighed and reserved for morphological analysis and

identification of mineralogy via XRD. The reaction was terminated at 10 to 25 minutes, by filtering, drying, and weighing of the remaining sample. Equimolar calcium and carbonate source concentrations equaling 0.2 *M* in the mixed reactant solution, using a plain Milli-Q solute and a reaction time of 5 minutes produced the greatest ratio of vaterite to calcite and was therefore chosen for trace element incorporation experiments.

2.5. Calculation of partition coefficients

Partitioning of trace elements into the precipitate was determined for both the whole precipitate and the vaterite portion of the precipitate. The partition coefficient (D_{TE}) for an individual trace element incorporated into a mineral phase is defined as:

$$D_{TE} = (m_{TE} / m_{Ca^{2+}})_{solid} / (a_{TE} / a_{Ca^{2+}})_{av}$$

where $(m_{TE} / m_{Ca^{2+}})_{solid}$ is the ratio of molar concentrations of the trace element and Ca^{2+} in the solid and $(a_{TE} / a_{Ca^{2+}})_{av}$ is the average of the initial and final trace element to Ca^{2+} activity ratios in the liquid (Dromgoole and Walter, 1990). Because activity coefficients for the examined trace elements and Ca^{2+} in the liquid have been shown to be nearly equal (Dromgoole and Walter, 1990), molar concentrations were used in place of activities, yielding the equation:

$$D_{TE} = (m_{TE} / m_{Ca^{2+}})_{solid} / (m_{TE} / m_{Ca^{2+}})_{av}$$

Partitioning of trace elements was determined for both the whole experiments and for the vaterite portion of the precipitate. Trace element partitioning into the vaterite portion of the precipitate was then determined by mass balance, using published calcite partition coefficients for the same elements, experimentally

Table 4. Published partition coefficients values (D_{TE}) for experimentally precipitated calcite.

D_{TE} calcite*	Reference*	T°C	Technique	Comments
Mg^{2+}				
0.012 - 0.032	Mucci and Morse, 1983	25	chemo-stat	Increased $D_{Mg^{2+}}$ with increased Mg/Ca and decreased precipitation rate; in seawater solutions
0.012 - 0.027	Mucci, 1998	5 - 40	chemo-stat	Increased $D_{Mg^{2+}}$ with increased T
0.057	Katz, 1973	25	free-drift	Heterogeneous Mg^{2+} distribution
0.031 - 0.071	Sawada et al., 1990	25	free-drift	$D_{Mg^{2+}}$ for calcite formed rapidly by transformation of ACC; increasing Mg^{2+} incorporation with decreasing precipitation rate
Sr^{2+}				
0.08 - 0.4	Kitano et al., 1971	20	free-drift	Increased $D_{Sr^{2+}}$ in presence of citrate and/or increased Mg^{2+} incorporation; rapid precipitation experiments
0.14 - 0.08	Holland, 1964	25 - 100		Decreased $D_{Sr^{2+}}$ with increased T
0.055 - 0.059	Katz, 1973	40	chemo-stat	Increased $D_{Sr^{2+}}$ with increased precipitation rate
0.03 - 0.1	Lorens, 1981	25	chemo-stat	Increased $D_{Sr^{2+}}$ with increased precipitation rate
0.146 - 0.33	Mucci and Morse, 1983	25	chemo-stat	Increased $D_{Sr^{2+}}$ with increased Mg^{2+} incorporation
0.2 - 0.06	Pingatore et al., 1986	25	chemo-stat	Decreased $D_{Sr^{2+}}$ with increased Sr^{2+} ; decreased $D_{Sr^{2+}}$ with Ba^{2+} incorporation
Mn^{2+}				
3.8 - 16	Dromgoole and Walter, 1990	10 - 50	chemo-stat	Increased $D_{Mn^{2+}}$ with decreased precipitation rate or increased T
1 - 18	Pingatore et al., 1988	25	chemo-stat	Increased $D_{Mn^{2+}}$ with decreased precipitation rate
0 - 50	Lorens, 1981		chemo-stat	Increased $D_{Mn^{2+}}$ with decreased precipitation rate
Fe^{2+}				
3.7	Dromgoole and Walter, 1990	10 - 50	chemo-stat	Increased $D_{Fe^{2+}}$ with decreased precipitation or increased T; calcite precipitation inhibited at high Fe/Ca

* Holland (1964), Mucci and Morse (1983), Sawada et al. (1990), and Mucci (1998) calculate partition coefficients based on the standard model: $D_x = (m_x/m_{ca})_s / (m_x/m_{ca})_l$. Lorens (1981) and Pingatore et al. (1986) use a derivation of the Doerner-Hoskins model for calculation of partition coefficients: $k_x = \log(x_l/x_i) / \log(Ca_l/Ca_i)$, which accounts for changing composition of fluids and precipitates during the experiment. Dromgoole and Walter (1990) calculate distribution coefficients by the equation: $D_x = (m_x/m_{ca})_s / (m_x/m_{ca})_{ave}$ —a form similar to the homogeneous distribution law which is appropriate for homogeneous solids precipitated rapidly from a homogeneous fluid, but which does not imply equilibrium precipitation.

determined under similar low temperature conditions (Table 3) (Dromgoole and Walter, 1990; Sawada et al, 1990; Lorens, 1981). To calculate the partition coefficient for incorporation of a particular trace element into the vaterite portion of the precipitate the following equation was used:

$$D_{TE(vaterite)} = [D_{TE(total)} - (D_{TE(calcite)} \times f_{(calcite)})] / f_{(vaterite)}$$

where $D_{TE(total)}$ is the partition coefficient for the total precipitate and f is the fraction of vaterite or calcite in the binary system. Potential adsorption of trace metals onto the crystal surfaces (Rimstidt et al., 1998; Morse and Bender, 1990) was not taken into account in calculating partition coefficients from chemical data. All precipitate reserved for elemental analysis was rinsed during filtration to aid in dislodging potential adsorbed metals. Furthermore, in similar experiments, Dromgoole and Walter (1990) found adsorption of Mn^{2+} and Fe^{2+} on the surface of calcite crystals to be insignificant in calculation of partition coefficients.

3. Results

3.1. Reaction behavior

In each experiment, the addition of the carbonate source solution caused an immediate shift in solution pH, the extent of which increased with increasing reactant concentration. In experiments using equimolar, 0.2 M calcium and carbonate source solutions, the addition of the NaHCO₃ solutions resulted in a decrease in pH from initial values of 7 to approximately 6.8; by contrast, the addition of Na₂CO₃ solutions resulted in an increase in pH of values to approximately 9.9. Carbonate precipitation, as indicated by clouding of the solution, occurred concurrently with this pH shift.

When Na₂CO₃ was used as the carbonate source, most aliquots taken immediately upon mixing of the reactants were gelatinous in consistency, which is interpreted to reflect initial precipitation of amorphous calcium carbonate (ACC) (Sawada et al., 1990; Andreassen, 2005). A rapid drop in solution pH of approximately 1 pH unit occurred between minutes two and three, during which the reaction product lost its gelatinous consistency. This transition is interpreted to signal the transformation of the ACC to either calcite, vaterite, or a mixture of the two (Sawada et al., 1990; Andreassen, 2005).

Exceptions to this reaction behavior occurred when Mg²⁺-doped solutions were reacted with Na₂CO₃ carbonate source solutions. At all Mg²⁺ concentrations (1, 2, and 5 times modern seawater), mixing of reactants immediately produced a viscous gel that was unable to be filtered. At low Mg²⁺ concentrations, the reaction product maintained this gelatinous consistency for >72 hours. At Mg²⁺ concentrations 2x and

5x present seawater, the gel separated into distinct precipitate and solution phases in <24 hours. Aliquots of all concentrations reverted to liquid when placed into the oven and a formed a new precipitate of significantly smaller volume.

3.2. Results of trace element incorporation

Mg²⁺ incorporation

The results of Mg²⁺ experiments are summarized in Tables 2 and 3, and Figure 12. $D_{Mg^{2+}}$ values for experimentally precipitated vaterite were investigated for Mg²⁺ concentrations equal to 1x, 2x, and 5x present seawater value of 53.2 mM (Millero and Sohn, 1992) in 0.2 M Ca²⁺ and carbonate source solutions. These Mg²⁺ concentrations correspond to $m_{Mg^{2+}}/m_{Ca^{2+}}$ ratios of 0.266, 0.532, and 1.33 respectively. No vaterite was formed in Na₂CO₃ reaction solutions; upon mixing of reagents a colloidal substance was produced that was unable to be filtered. The partition coefficient for the colloid increased from 0.059 to 0.140 with increasing Mg²⁺ concentration. When the colloid was placed into the oven, it dissolved and reprecipitated as calcite and one or more unidentified mineral phases. For NaHCO₃ reactions, percent abundance vaterite produced ranged from 66.7% to 86.3%; at the highest Mg²⁺ concentration, a duplicate run produced no vaterite. Calculated partition coefficients in NaHCO₃ solutions ranged from 0.005 to 0.039 for vaterite (0.009 to 0.042 for total NaHCO₃ precipitate) with a trend of increasing $D_{Mg^{2+}}$ with increasing Mg²⁺ concentration.

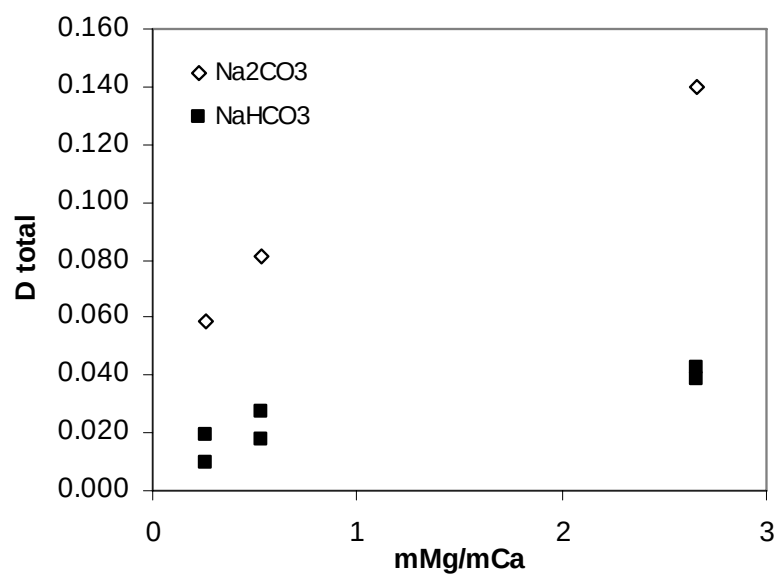


Figure 12. Mg^{2+} incorporation into the total precipitate increased with increasing $m_{\text{Mg}^{2+}}/m_{\text{Ca}^{2+}}$. Partition coefficients for the total precipitate are shown because no vaterite was produced in reactions in which Na_2CO_3 was used as the carbonate source.

Sr²⁺ incorporation

Sr²⁺ incorporation into experimentally precipitated vaterite was investigated for 1x, 2x, and 10x present seawater value of 90 μM (Millero and Sohn, 1992) using 0.2 M Ca²⁺ and carbonate source solutions at 22°C (results summarized in Tables 2 and 3, and Figure 13). These Sr²⁺ concentrations correspond to $m_{\text{Sr}^{2+}}/m_{\text{Ca}^{2+}}$ ratios of 4.5×10^{-4} , 9.0×10^{-4} , and 4.5×10^{-3} , respectively. The percent abundance vaterite produced in Na₂CO₃ reactions ranged 59.9 to 78.6% and calculated $D_{\text{Sr}^{2+}}$ values for vaterite ranged from 0.21 to 0.33 (0.18 to 0.27 for total precipitate). In NaHCO₃ carbonate source experiments, the fraction of vaterite generated during reactions increased from 76.3 to 93.6% with increasing Sr²⁺ concentration; the calculated partition coefficients ranged from 0.23 to 0.36 (0.22 to 0.29 for total precipitate). There was no apparent trend for increasing $D_{\text{Sr}^{2+}}$ with increasing Sr²⁺ concentrations in either Na₂CO₃ or NaHCO₃ experiments.

Mn²⁺ incorporation

Mn²⁺ incorporation into vaterite was investigated for $m_{\text{Mn}^{2+}}/m_{\text{Ca}^{2+}}$ ratios of 0.001, 0.01, and 0.05, with 0.2 M Ca²⁺ and carbonate source solutions. For Na₂CO₃ reaction solutions, the percent abundance of vaterite produced decreased from 81.5% to 14.6% with increasing Mn²⁺ concentrations; Mn²⁺ incorporation into the vaterite portion similarly decreased from $D_{\text{Mn}^{2+}} = -1.46$ to -80.37. For NaHCO₃ reaction solutions, an average of 89% vaterite was produced at the lowest Mn²⁺ concentration and higher concentrations produced no vaterite. Incorporation of Mn²⁺ into the total

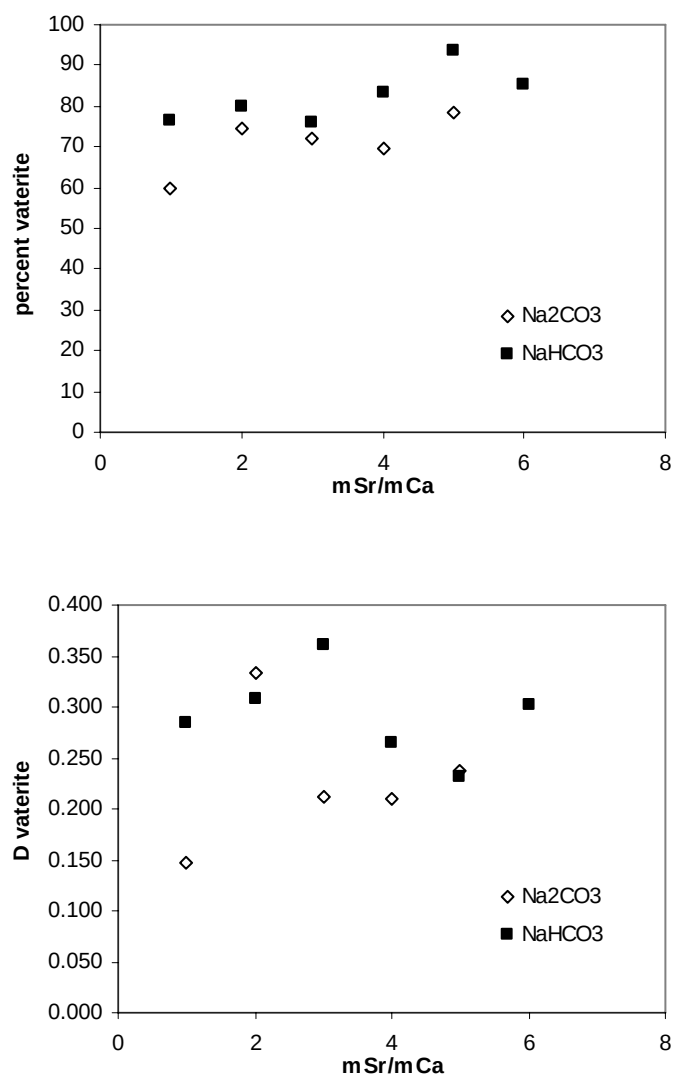


Figure 13. The percent vaterite produced in experiments with added Sr^{2+} increased with increasing $m_{\text{Sr}^{2+}}/m_{\text{Ca}^{2+}}$ (top). No trend is evident for change in Sr^{2+} incorporation into vaterite with changing $m_{\text{Sr}^{2+}}/m_{\text{Ca}^{2+}}$ (bottom).

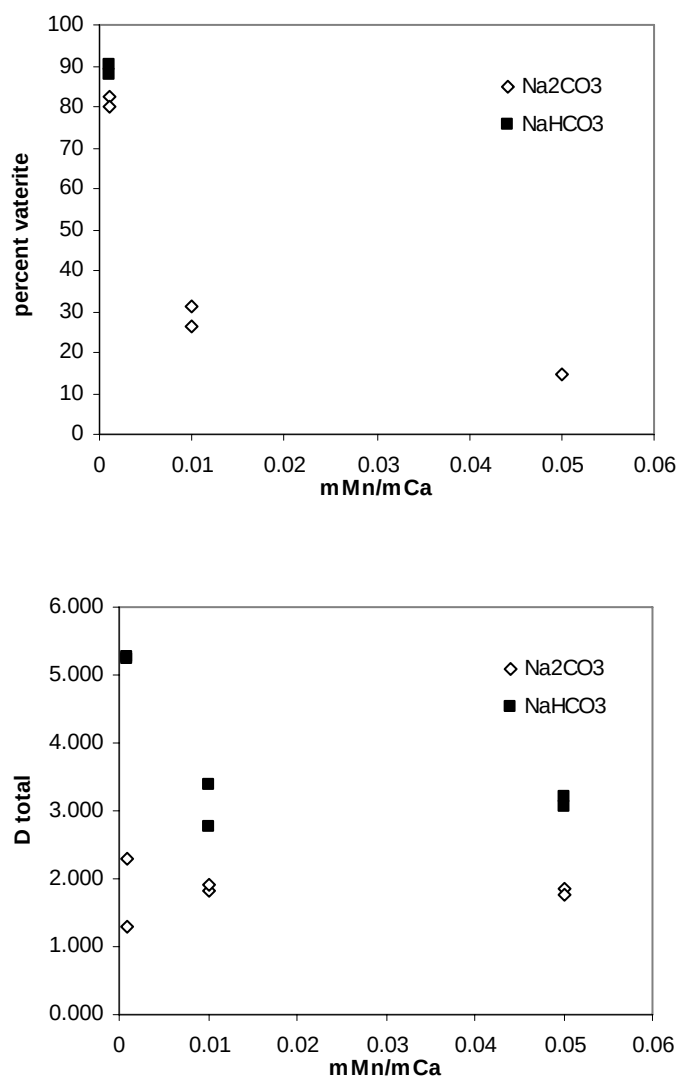


Figure 14 Mn^{2+} incorporation experiments showed a strong decrease in percent vaterite produced with increasing $m_{\text{Mn}^{2+}}/m_{\text{Ca}^{2+}}$ (top), although no volume change in the total precipitate occurred. Partitioning of Mn^{2+} into the entire precipitate decreased with increasing $m_{\text{Mn}^{2+}}/m_{\text{Ca}^{2+}}$ as well (bottom). D_{TE} for the entire precipitate is shown because no vaterite was produced in NaHCO_3 experiments at moderate- to high $m_{\text{Mn}^{2+}}/m_{\text{Ca}^{2+}}$.

solid in NaHCO_3 experiments decreased from 2.30 to 1.76 with increasing Mn^{2+} concentrations; the calculated partition coefficient for the vaterite produced in 0.001 reaction solution was 5.27.

Fe^{2+} incorporation

Fe^{2+} incorporation into vaterite was explored in 0.2 M Ca^{2+} and carbonate source solutions for $m_{\text{Mn}^{2+}}/m_{\text{Ca}^{2+}}$ ratios of 0.001, 0.01, and 0.05. $D_{\text{Fe}^{2+}}$ values for experiments in which Na_2CO_3 was used as the carbonate source range from -3.49 to 0.95 for vaterite (0.77 to 1.69 for total precipitate), with no apparent correlation to Fe^{2+} concentrations. The percent abundance vaterite produced in these experiments varied from 40.8% to 83.9%, although at an $m_{\text{Fe}^{2+}}/m_{\text{Ca}^{2+}}$ ratio of 0.01, duplicate experiments produced a 51% difference in the percent abundance vaterite. In NaHCO_3 reaction solutions, duplicate experiments at an $m_{\text{Fe}^{2+}}/m_{\text{Ca}^{2+}}$ ratio equal to 0.001 produced 90.4% and 83.8% abundance vaterite; however, no vaterite was produced at higher Fe^{2+} concentrations. $D_{\text{Fe}^{2+}}$ for the whole precipitate ranged from 2.00 to 5.70 and increased with increasing Fe^{2+} concentrations. The calculated $D_{\text{Fe}^{2+}}$ value for vaterite produced at $m_{\text{Fe}^{2+}}/m_{\text{Ca}^{2+}}$ 0.001 is 1.83.

4. Discussion

4.1. Trace element incorporation

Three mechanisms are described by McIntire (1963) to account for the ways in which trace elements can be incorporated into a mineral precipitating from a solution: 1) adsorption at the crystal surface; 2) occlusion either of adsorbed trace elements, small crystals of a different phase, or fluid inclusions and; 3) solid solution. Because solid solution is generally considered an equilibrium phenomenon and can be described in thermodynamic terms it is the simplest of the three to determine. Even solid solution substitution can be complicated, however, because the coordination of the foreign ion and whether it resides in a lattice or non-lattice position are determined by a combination of ionic radius and precipitation rate (Pingatore and Eastman, 1986). At very high precipitation rates, adsorption, occlusion, and an increase in lattice defects are likely to occur (Bunsenburg and Plummer, 1985; Pingatore and Eastman, 1986, Watson, 2004), all of which generate variable partition coefficient values that are often applicable only for the particular conditions studied (Rimstidt et al., 1998, Watson, 2004).

As a result, there is both controversy regarding reported trace element partition coefficient values for carbonate minerals (Table 4; see Rimstidt et al., 1998 for a review) and confusion as to which apply to particular geologic settings (Morrow and Mayers 1978a, b, 1980; Veizer, 1978, 1983; Pingatore, 1978, 1980; Angus et al., 1979, Morse and Bender, 1990). The wide range in D_{TE} carbonate values calculated from experimental procedure can be attributed to the many parameters that affect the

kinetics of carbonate precipitation and thereby determine to what extent trace elements are incorporated into lattice defects rather than directly into the lattice structure (McIntire, 1963; Angus et al., 1979; Bunsenburg and Plummer, 1985; Pingatore and Eastman, 1986; Clarkson, 1992; Rimstidt et al., 1998; Teng et al., 2000; Watson, 2004). Experimental calcite precipitation studies have found that the ratio of the trace element to Ca^{2+} (Dromgoole and Walter, 1990; Zhong and Mucci, 1989, 1995), salinity and specific ion concentrations (Mucci and Morse, 1983; Pingatore and Eastman, 1986; Zhong and Mucci 1989; Davis et al., 2000; Curti et al., 2005), solution pH (Curti et al., 2005), temperature (Bottcher, 1998; Mitchell and Ferris, 2005), carbonate saturation (Lorens, 1981; Mucci and Morse, 1983; Pingatore et al., 1988; Tesoriero and Pankow, 1996), and the addition of organic molecules (Mitchell and Ferris, 2005) each effect the mechanism and amount by which trace elements are incorporated into a calcite crystal (see Rimstidt et al., 1998).

Whereas the results presented here do not likely reflect equilibrium values for D_{TE} , they do provide new information on trace element incorporation into rapidly precipitated carbonate phases and the influence of individual metals on precipitate mineralogy. This information will be useful, in particular, when evaluating trace element distribution in cores vs. overgrowths of Precambrian molar-tooth microspar.

The principal disadvantage to experimental methods presented here is that calculation of trace element incorporation into vaterite depends on assumed D_{TE} values for calcite, which varies widely (see Table 4; McIntire, 1963; Morse and Bender, 1990; Rimstidt et al., 1998). Furthermore, in precipitation experiments, reaction solutions become increasingly depleted in ions as the solid phase forms,

causing activity ratios of chemical species in both phases change incrementally (Morse and Bender, 1990). To address this problem, many studies employ “chemo-stat” conditions to replenish solution chemicals (see Table 4); chemo-stat conditions, however, are difficult to achieve in rapid precipitation experiments. The potential for oscillatory zoning and mineralogical heterogeneity within a single crystal is high in “free-drift” experiments (i.e. reaction solutions are allowed to evolve; see Table 4; this study) and Morse and Bender (1990) suggest caution when applying these partition coefficients to geologic settings.

Because natural fluids are chemically complex, several authors have investigated the effects of combined chemical species on trace element incorporation into carbonate minerals (see Table 4). These studies have found that 1) competition or cooperation between cations can effect incorporation, for example, the presence of Mn^{2+} and Mg^{2+} in solution promotes incorporation of Sr^{2+} into the calcite crystal lattice (Ichikuni, 1973; Carpenter and Lohmann, 1992); 2) ionic interactions and in reaction solutions effect diffusion; Pingatore et al. (1986) showed that relatively high concentrations of Na^+ in solution depresses Sr^{2+} diffusion and incorporation into calcite; and 3) the presence of certain ionic species (i.e. Fe^{2+} and SO_4^{2-}) can inhibit carbonate precipitation entirely (Dromgoole and Walter, 1990;). Each of these potential mechanisms for change in trace element incorporation must be considered when applying partition coefficients to geologic materials.

Mg²⁺ incorporation

Incorporation of Mg²⁺ into vaterite in NaHCO₃ solutions is considerably less than values of D_{Mg2+} (0.042 to 0.083) reported by Sawada et al. (1990) for vaterite formed by the transformation of ACC. When considering Mg²⁺ incorporation into the total mixture of calcite and vaterite precipitated in NaHCO₃ solutions, values (D_{total} = 0.009 – 0.042) are similar to those reported by Sawada et al. (1990) in Milli-Q water solutions (0.031 – 0.071) and Mucci and Morse (1982) in seawater solutions (0.012 – 0.032; 1982) for calcite. Mucci and Morse (1982) observed that above at low (< ~7.5) m_{Mg2+}/m_{Ca2+} solution ratios, incorporation of Mg²⁺ increases exponentially with decreasing m_{Mg2+}/m_{Ca2+}; the opposite trend was observed in these experiments, and the D_{total} measured here does not fall on the same exponential function fit to their data. The experiments of Sawada et al. (1990) also show that Mg²⁺ incorporation decreases with increasing Ca²⁺ and Mg²⁺ concentrations. The exception to this is the very rapid precipitation of ACC, which increased with increasing Ca²⁺, but not Mg²⁺ concentration (Sawada et al., 1990); similar behavior, at the same rate of change of incorporation, was observed in this study with increasing Mg²⁺ although absolute D_{TE} values do not overlap. This suggests that under conditions of high saturation and rapid precipitation, such as those proposed for the origins of MT microspar, one should expect to find elevated concentrations of Mg²⁺.

In this study, up to 11 times more Mg²⁺ was incorporated into the colloid material produced in Na₂CO₃ solutions than is reported for other carbonate precipitation experiments (Katz, 1973; Mucci and Morse, 1983; Zhong and Mucci, 1989; Mucci, 1988; Hartley and Mucci, 1996), and much closer to ACC experiments

of Sawada et al. (1990) whose reported $D_{\text{Mg}^{2+}}$ values are only 1.8 times lower for precipitation of ACC and 1.6 times lower for precipitation of vaterite. This observation may have important implications for the formation of Precambrian MT microspar: enrichment in Mg^{2+} in this colloid substance is consistent with qualitative SIMS ion imaging that suggests that spheroidal cores of MT microspar are enriched in Mg^{2+} and the increase in viscosity such a phase would help maintain the competency of MT voids during precipitation and lithification.

Sr^{2+} incorporation

Values calculated for Sr^{2+} incorporation into vaterite in this study are up to 7 times higher than reported values for Sr^{2+} incorporation into experimentally precipitated calcite (Holland et al., 1964; Katz et al., 1972; Lorens, 1981; Mucci and Morse, 1982; Pingatore and Eastman, 1986), but less than that reported for Sr^{2+} incorporation into experimental aragonite (Holland et al., 1963). There is uncertainty, however, in the absolute values for $D_{\text{Sr}^{2+}(\text{vaterite})}$, because the value used for $D_{\text{Sr}^{2+}(\text{calcite})}$ (0.1; Lorens, 1981) in the mass balance equation is likely underestimated. Whereas most values reported for Sr^{2+} incorporation into calcite range from 0.01 to 0.14, Kitano et al. (1971) report $D_{\text{Sr}^{2+}}$ values of up to 0.4 for calcite precipitated spontaneously in solutions of high carbonate saturation, suggesting that lattice defects associated with rapid precipitation may substantially increase Sr^{2+} incorporation. In this study, Sr^{2+} incorporation into the total precipitate increases as the percent abundance vaterite increases. It is unclear, however, if this is because vaterite incorporates higher concentrations of Sr^{2+} into its crystal structure than does calcite,

or if increased amounts of Sr^{2+} are incorporated into calcite with the fast precipitation rate of these experiments. The former explanation is more likely, as the volume of precipitate generated remains constant in all Sr^{2+} experiments, indicating that precipitation rate is unchanged.

Mn^{2+} and Fe^{2+} incorporation

Although Mn^{2+} and Fe^{2+} are common trace elements in carbonate rocks (Hemming et al., 1989; Savard et al., 1995) their incorporation occurs predominantly during postdepositional alteration of primary marine carbonate phases. Because Mn and Fe are only soluble in their reduced state, their concentration in oxidized fluids is generally insignificant. The environment of formation for Proterozoic MT microspar is primarily in the shallow substrate (James et al., 1998; Pratt et al., 1998), which may have contained lower oxygen concentrations than overlying seawater. Microspar cores and overgrowth show luminescent characteristics in CL distinct from that of overgrowths (Crawford et al., 2005; Bishop et al., 2006a,b; Pollock et al., 2006), which is attributed to differential Mn-Fe incorporations (Hemming et al., 1989; Savard et al., 1995). Therefore partitioning of Fe^{2+} and Mn^{2+} into vaterite may be relevant in evaluating its plausibility as the initial mineralogy of MT microspar.

While care was taken to maintain an oxygen-free atmosphere in the reaction vessel during Mn^{2+} and Fe^{2+} experiments, exposure of the precipitate to the atmosphere during filtration and drying could not be avoided. Therefore, oxidation may have affected precipitate mineralogy.

This study has shown that increasing $m_{\text{Mn}^{2+}}/m_{\text{Ca}^{2+}}$ favors the transformation of ACC to calcite, rather than to vaterite. This, in combination with the trend of decreasing $D_{\text{Mn}^{2+}}$ in total precipitate, is consistent with data that show less Mn^{2+} is incorporated with increasing calcite precipitation rate (Lorens 1981, Pingitore et al. 1988; Dromgoole and Walter 1990). Mn^{2+} incorporation into rapidly precipitated carbonate phases explored here is extraordinarily low when compared with published values, which suggests Mn^{2+} incorporation in these experiments may be controlled by the increased precipitation rate, rather than individual mineralogy.

Consistent results in both mineralogy and $D_{\text{Fe}^{2+}}$ were obtained in duplicate experiments at low Fe^{2+} concentrations at a range of pH values. Considerably more vaterite precipitation occurred at low pH values and increasing Fe^{2+} concentration appears to favor the formation of calcite over vaterite. As is the case with Mn^{2+} , this study shows the inhibitive effect of increasing Fe^{2+} concentrations on vaterite formation although increasing $m_{\text{Fe}^{2+}}/m_{\text{Ca}^{2+}}$ did not inhibit overall precipitation in alkaline solutions. This observation is inconsistent with the findings of Dromgoole and Walter (1990) that the presence calcite precipitation is inhibited at $m_{\text{Fe}^{2+}}/m_{\text{Ca}^{2+}}$ ratios of 0.01 and 0.05, although this may simply be because their reactions occurred in solutions containing half the reactant concentration of this study.

4.2. Implications for interpreting MT microspar

The sedimentological character of molar-tooth structures requires rapid precipitation of carbonate within newly formed voids to prevent void collapse or significant sediment infill within the unlithified substrate. Vaterite has been

proposed as a possible mineralogical precursor to MT microspar because microspar cores appear to have precipitated initially as an unstable mineralogy which then rapidly underwent varying degrees of potentially rapid morphological transformation (Crawford, 2005). Similar behavior has been observed in vaterite precipitation experiments (Kralj et al. 1994, 1997, Abdel- Aal and Sawada, 2003; this study).

Although most carbonate precipitation experiments do not achieve equilibrium, care must be taken when applying experimentally derived partition coefficients to geologic carbonates (McIntire, 1963; Morse and Bender, 1990; Rimstidt et al., 1998). Also, because the results of precipitation experiments presented here are not static, partition coefficients do not account for potential changes in solid and solution composition during the experimental run. As such, partition coefficients reported here may not have broad geologic application. However, petrographic analysis of MT microspar suggests potential for similarly static precipitation conditions: because this unusual precipitate is largely constrained to voids that might have formed up to 1 m beneath the sediment-water interface, it is unlikely that active replenishment of ions would have occurred during microspar precipitation (James et al., 1998; Pratt et al., 1998; Bishop et al., 2006a,b). Even in an open water environment, precipitation rates experienced here would likely be greater than mixing rates within the water column. Therefore, partition coefficients reported here are likely valid for comparison MT microspar and other rapidly precipitated carbonate phases.

The precipitation of a colloid-like gel in Na_2CO_3 experiments show the inhibiting effect of Mg^{2+} on vaterite formation in solutions in which CO_3^{-2} is the

dominant carbonate species. The partition coefficient values for Mg^{2+} incorporation in the total colloidal substance are similar to those determined by Sawada et al. (1990) for ACC, and slightly higher than those determined for calcite formed rapidly by transformation of the ACC. This elevated incorporation of Mg^{2+} , in combination with the relative stability of the colloid, is consistent with either an originally vaterite mineralogy for MT microspar or initial precipitation of an amorphous phase (see Part I)- pore fluids in Precambrian ocean sediments may have been concentrated, relative to modern, in DIC (Grotzinger, 1990; Grotzinger and Kasting, 1993; Bartley and Kah, 2005) and Mg^{2+} (Tucker 1982; Grotzinger, 1989; Kah et al., 2001). It is therefore plausible that a rapidly precipitated, highly viscous colloidal substance was produced in MT structures in fluids similar to experimental solutions. Such a phase would help maintain the structure of MT voids and prevent sediment infill.

Sr^{2+} incorporation into experimentally precipitated carbonates is elevated when compared with studies investigating incorporation into calcite at low precipitation rates (Holland et al., 1964; Katz et al., 1972; Lorens, 1981; Mucci and Morse, 1982; Pingatore and Eastman, 1986), yet are low when compared with aragonite $D_{\text{Sr}^{2+}}$ (Crawford, 2005; Holland, 1963). This is consistent with trace element image analysis of MT microspar that shows Sr^{2+} concentrated in overgrowths (Crawford, 2006). Mn^{2+} has been shown to promote luminescence in carbonate minerals examined using cathodoluminescent (CL) microscopy (Hemming et al., 1989). MT cores are only dully luminescent- to extinct in CL (Crawford, 2005; Bishop et al., 2006b; Pollock et al., 2006), indicating low concentrations of the Mn^{2+} ion, which is consistent with these results of experimental precipitation that show low

concentrations of Mn^{2+} incorporation into rapidly precipitated carbonate. These experiments show that Mn^{2+} incorporation is substantially less (up to 28 times) in rapidly precipitated carbonates than at slower precipitation rates achieved in other experimental studies (Lorens, 1981; Pingatore et al., 1988; Dromgoole and Walter, 1990). Potentially, MT microspar crystals rapidly nucleated and grew as vaterite or calcite, excluding Mn^{2+} from the crystal structure until ion supply in the fluids became limited and chemically distinct overgrowth precipitation initiated with increased incorporation of Mn^{2+} .

5. Conclusions

Results of this study show the partition coefficients for trace elements Mg^{2+} , Sr^{2+} , Fe^{2+} and Mn^{2+} into rapidly precipitated carbonate phases at 20°C and the effects of these elements on precipitate mineralogy. Trace element incorporation is largely a function of precipitation rate and therefore the results of these experiments deviate from previously reported values in carbonate phases. However, the experimental conditions investigated here are likely a good comparison with geologic examples of MT microspar, which have been independently shown to result from rapid precipitation under ion-limited conditions.

Results show that elevated Mg^{2+} and depressed Sr^{2+} and Mn^{2+} incorporation into vaterite, and into the total precipitate generated, are consistent with qualitative analysis of these elements in MT microspar. Furthermore, it was shown that the presence of Mg^{2+} in solutions of high carbonate saturation promote precipitation of a colloidal substance, ideal to maintain MT structure competency in Proterozoic shallow marine sediments. These data then, are an important tool for evaluating the plausibility of vaterite as the precursor mineralogy to spatially and temporally restricted MT microspar and may therefore provide a critical link in deciphering the relationship between carbonate precipitation and Precambrian marine geochemistry.

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Appendix

Table A.1. Reactant solution concentration and total reaction solution concentration for individual experiments.

Experiment ID	Solute	Ca ²⁺ source	Ca ²⁺ source solution volume (mL)	Ca ²⁺ source solution (moles/L)	Trace element moles/L in Ca ²⁺ source solution	CO ₃ ²⁻ source	CO ₃ ²⁻ source solution volume (mL)	CO ₃ ²⁻ source solution (moles/L)	Ca ²⁺ and CO ₃ ²⁻ moles/L final reaction solution	Trace element moles/L final reaction solution
3a	SW	CaCl ₂	175.68	0.076		Na ₂ CO ₃	19.52	0.512	0.1	
6a	SW	CaCl ₂	341.6	0.157		Na ₂ CO ₃	50	0.800	0.2	
7a	SW	CaCl ₂	341.6	0.235		Na ₂ CO ₃	50	1.200	0.3	
.01	NaCl, I=0.7	CaCl ₂	280	0.014		Na ₂ CO ₃	20	0.150	0.01	
.03b	NaCl, I=0.7	CaCl ₂	280	0.036		Na ₂ CO ₃	20	0.375	0.03	
.06	NaCl, I=0.7	CaCl ₂	220	0.091		Na ₂ CO ₃	30	0.500	0.06	
.1	NaCl, I=0.7	CaCl ₂	220	0.152		Na ₂ CO ₃	30	0.834	0.1	
.2	NaCl, I=0.7	CaCl ₂	220	0.304		Na ₂ CO ₃	30	1.863	0.2	
.2b	I=0.5	CaCl ₂	220	0.304		Na ₂ CO ₃	30	1.863	0.2	
.2d	fsw, I=7	CaCl ₂	220	0.304		Na ₂ CO ₃	30	1.863	0.2	
.25	fsw, I=.7	CaCl ₂	220	0.380		Na ₂ CO ₃	30	2.084	0.25	
.2c	MQ	CaCl ₂	220	0.304		Na ₂ CO ₃	30	1.863	0.2	
.25b	MQ	CaCl ₂	220	0.380		Na ₂ CO ₃	30	2.084	0.25	
bc.1	MQ	CaCl ₂	210	0.159		NaHCO ₃	40	0.625	0.1	
bc.15	MQ	CaCl ₂	220	0.228		NaHCO ₃	30	1.250	0.15	
bc.2	MQ	CaCl ₂	210	0.319		NaHCO ₃	40	1250.000	0.2	

Table A.1. Continued.

Experiment ID	Solute	Ca ²⁺ source	Ca ²⁺ source solution volume (mL)	Ca ²⁺ source solution (moles/L)	Trace element moles/L in Ca ²⁺ source solution	CO ₃ ²⁻ source	CO ₃ ²⁻ source solution volume (mL)	CO ₃ ²⁻ source solution (moles/L)	Ca ²⁺ and CO ₃ ²⁻ moles/L final reaction solution	Trace element moles/L final reaction solution
bc.2b	MQ	CaCl ₂	210	0.319		NaHCO ₃	40	1.250	0.2	
bc.25	MQ	CaCl ₂	210	0.398		NaHCO ₃	40	1.563	0.25	
bc.3	MQ	CaCl ₂	210	0.273		NaHCO ₃	40	1.407	0.3	
x.2	MQ	CaCl ₂	220	0.304		Na ₂ CO ₃	30	2.104	0.2	
xbc.2	MQ	CaCl ₂	200	0.334		NaHCO ₃	50	1.000	0.2	
Sr-bc-P(1)	MQ	CaCl ₂	115	0.349	6.75E-05	NaHCO ₃	35	0.857	0.2	5.18E-05
Sr-bc-P(2)	MQ	CaCl ₂	115	0.349	1.17E-04	NaHCO ₃	35	0.857	0.2	9.00E-05
Sr-bc-2x(1)	MQ	CaCl ₂	115	0.349	2.35E-04	NaHCO ₃	35	0.857	0.2	1.80E-04
Sr-bc-2x(2)	MQ	CaCl ₂	115	0.349	2.35E-04	NaHCO ₃	35	0.857	0.2	1.80E-04
Sr-bc-10x(1)	MQ	CaCl ₂	115	0.349	1.17E-03	NaHCO ₃	35	0.857	0.2	9.00E-04
Sr-bc-10x(2)	MQ	CaCl ₂	115	0.349	1.17E-03	NaHCO ₃	35	0.857	0.2	9.00E-04
Sr-c-Pc(1)	MQ	CaCl ₂	55	0.365	5.86E-05	Na ₂ CO ₃	20	0.750	0.2	4.29E-05
Sr-c-Pc(2)	MQ	CaCl ₂	55	0.365	1.22E-04	Na ₂ CO ₃	20	0.750	0.2	8.98E-05
Sr-c-2xc(1)	MQ	CaCl ₂	55	0.365	2.46E-04	Na ₂ CO ₃	20	0.750	0.2	1.80E-04

Table A.1. Continued.

Experiment ID	Solute	Ca ²⁺ source	Ca ²⁺ source solution volume (mL)	Ca ²⁺ source solution (moles/L)	Trace element moles/L in Ca ²⁺ source solution	CO ₃ ²⁻ source	CO ₃ ²⁻ source solution volume (mL)	CO ₃ ²⁻ source solution (moles/L)	Ca ²⁺ and CO ₃ ²⁻ moles/L final reaction solution	Trace element moles/L final reaction solution
Sr-c-2xc(2)	MQ	CaCl ₂	55	0.365	2.46E-04	Na ₂ CO ₃	20	0.750	0.2	1.80E-04
Sr-c-10xc(1)	MQ	CaCl ₂	55	0.365	1.23E-03	Na ₂ CO ₃	20	0.750	0.2	9.00E-04
Sr-c-10xc(2)	MQ	CaCl ₂	55	0.365	1.23E-03	Na ₂ CO ₃	20	0.750	0.2	9.00E-04
Mg-c-P	MQ	CaCl ₂	55	0.365	7.35E-02	Na ₂ CO ₃	20	0.750	0.2	5.39E-02
Mg-c-2x	MQ	CaCl ₂	55	0.365	1.47E-01	Na ₂ CO ₃	20	0.750	0.2	1.08E-01
Mg-bc-P(1)	MQ	CaCl ₂	115	0.349	1.48E-01	NaHCO ₃	35	0.857	0.2	1.13E-01
Mg-bc-P(2)	MQ	CaCl ₂	115	0.349	7.07E-02	NaHCO ₃	35	0.857	0.2	5.42E-02
Mg-bc-2x(1)	MQ	CaCl ₂	115	0.349	1.40E-01	NaHCO ₃	35	0.857	0.2	1.08E-01
Mg-bc-2x(2)	MQ	CaCl ₂	115	0.349	1.40E-01	NaHCO ₃	35	0.857	0.2	1.08E-01
Mg-bc-5x(1)	MQ	CaCl ₂	170	0.236	2.64E-01	NaHCO ₃	30	1.333	0.2	2.24E-01
Mg-bc-5x(2)	MQ	CaCl ₂	170	0.236	1.78E-01	NaHCO ₃	30	1.333	0.2	1.52E-01
Mn-bc-001c(1)	MQ	CaCl ₂	115	0.349	5.64E-05	NaHCO ₃	35	0.857	0.2	4.32E-05
Mn-bc-001c(2)	MQ	CaCl ₂	115	0.349	8.34E-05	NaHCO ₃	35	0.857	0.2	6.39E-05

Table A.1. Continued.

Experiment ID	Solute	Ca ²⁺ source	Ca ²⁺ source solution volume (mL)	Ca ²⁺ source solution (moles/L)	Trace element moles/L in Ca ²⁺ source solution	CO ₃ ²⁻ source	CO ₃ ²⁻ source solution volume (mL)	CO ₃ ²⁻ source solution (moles/L)	Ca ²⁺ and CO ₃ ²⁻ moles/L final reaction solution	Trace element moles/L final reaction solution
Mn-bc-01c(1)	MQ	CaCl ₂	115	0.349	1.68E-03	NaHCO ₃	35	0.857	0.2	1.29E-03
Mn-bc-01c(2)	MQ	CaCl ₂	115	0.349	1.68E-03	NaHCO ₃	35	0.857	0.2	1.29E-03
Mn-bc-05c(1)	MQ	CaCl ₂	115	0.349	8.34E-03	NaHCO ₃	35	0.857	0.2	6.39E-03
Mn-bc-05c(2)	MQ	CaCl ₂	115	0.349	8.34E-03	NaHCO ₃	35	0.857	0.2	6.39E-03
Mn-c-001c(1)	MQ	CaCl ₂	115	0.349	8.34E-05	Na ₂ CO ₃	35	0.857	0.2	6.39E-05
Mn-c-001c(2)	MQ	CaCl ₂	115	0.349	8.34E-05	Na ₂ CO ₃	35	0.857	0.2	6.39E-05
Mn-c-01c(1)	MQ	CaCl ₂	115	0.349	1.68E-03	Na ₂ CO ₃	35	0.857	0.2	1.29E-03
Mn-c-01c(2)	MQ	CaCl ₂	115	0.349	1.68E-03	Na ₂ CO ₃	35	0.857	0.2	1.29E-03
Mn-c-05c(1)	MQ	CaCl ₂	115	0.349	8.34E-03	Na ₂ CO ₃	35	0.857	0.2	6.39E-03
Mn-c-05c(2)	MQ	CaCl ₂	115	0.349	8.34E-03	Na ₂ CO ₃	35	0.857	0.2	6.39E-03
Fe-bc-001(1)	MQ	CaCl ₂	115	0.349	1.31E-04	NaHCO ₃	35	0.857	0.2	1.00E-04
Fe-bc-001(2)	MQ	CaCl ₂	115	0.349	1.31E-04	NaHCO ₃	35	0.857	0.2	1.00E-04
Fe-bc-01(1)	MQ	CaCl ₂	115	0.349	2.64E-02	NaHCO ₃	35	0.857	0.2	2.02E-02

Table A.1. Continued.

Experiment ID	Solute	Ca ²⁺ source	Ca ²⁺ source solution volume (mL)	Ca ²⁺ source solution (moles/L)	Trace element moles/L in Ca ²⁺ source solution	CO ₃ ²⁻ source	CO ₃ ²⁻ source solution volume (mL)	CO ₃ ²⁻ source solution (mole/L)	Ca ²⁺ and CO ₃ ²⁻ moles/L final reaction solution	Trace element moles/L final reaction solution
Fe-bc-01(2)	MQ	CaCl ₂	115	0.349	2.64E-02	NaHCO ₃	35	0.857	0.2	2.02E-02
Fe-bc-05(1)	MQ	CaCl ₂	115	0.349	1.31E-02	NaHCO ₃	35	0.857	0.2	1.00E-02
Fe-bc-05(2)	MQ	CaCl ₂	115	0.349	1.31E-02	NaHCO ₃	35	0.857	0.2	1.00E-02
Fe-c-001(1)	MQ	CaCl ₂	115	0.349	1.31E-04	Na ₂ CO ₃	35	0.857	0.2	1.00E-04
Fe-c-001(2)	MQ	CaCl ₂	115	0.349	1.31E-04	Na ₂ CO ₃	35	0.857	0.2	1.00E-04
Fe-c-01(1)	MQ	CaCl ₂	115	0.349	2.64E-02	Na ₂ CO ₃	35	0.857	0.2	2.02E-02
Fe-c-01(2)	MQ	CaCl ₂	115	0.349	2.64E-02	Na ₂ CO ₃	35	0.857	0.2	2.02E-02
Fe-c-05	MQ	CaCl ₂	115	0.349	1.31E-02	Na ₂ CO ₄	35	0.857	0.2	1.00E-02
org.1c	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	120	0.124		Na ₂ CO ₃	30	0.500	0.1	
org.1bc	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	120	0.124		NaHCO ₃	30	0.500	0.1	
org.2c	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	120	0.248		Na ₂ CO ₃	30	1.000	0.2	
org.2bc	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	120	0.248		NaHCO ₃	30	1.000	0.2	
sworg.1c	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	135	0.110		Na ₂ CO ₃	15	1.000	0.1	
sworg.1bc	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	130	0.114		NaHCO ₃	20	0.750	0.1	
sworg.2c	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	130	0.229		Na ₂ CO ₃	20	1.500	0.2	
sworg.2bc	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	120	0.248		NaHCO ₃	30	1.000	0.2	

Table A.2. Reactants, withdrawal times, precipitate volume and mineralogy for individual aliquots.

Sample ID	Solute	Ca ²⁺ source	CO ₃ ²⁻ source	Total Ca ²⁺ and CO ₃ ²⁻ reactant concentration	Aliquot withdrawal time (minutes)	Precipitate mass (g)	Aliquot volume (ml)	Precipitate mass per mL aliquot	% vaterite	% calcite
3a(5)X	SW	CaCl ₂	Na ₂ CO ₃	0.1	5	0.03	10.00	2.707	0	100
3a(10)X	SW	CaCl ₂	Na ₂ CO ₃	0.1	10	0.03	10.00	2.896	-	-
3a(15)X	SW	CaCl ₂	Na ₂ CO ₃	0.1	15	0.03	10.00	2.904	-	-
3a(20)X	SW	CaCl ₂	Na ₂ CO ₃	0.1	20	0.03	10.00	3.011	-	-
6a(10)	SW	CaCl ₂	Na ₂ CO ₃	0.2	10	0.24	20.00	12.087	-	-
6a(15)	SW	CaCl ₂	Na ₂ CO ₃	0.2	15	0.20	20.00	10.212	-	-
6a(20)	SW	CaCl ₂	Na ₂ CO ₃	0.2	20	0.20	20.00	9.981	-	-
6a(30)	SW	CaCl ₂	Na ₂ CO ₃	0.2	30	0.21	20.00	10.274	-	-
6a(40)	SW	CaCl ₂	Na ₂ CO ₃	0.2	40	0.21	20.00	10.296	-	-
6a(50)	SW	CaCl ₂	Na ₂ CO ₃	0.2	50	0.21	20.00	10.631	-	-
7a(10)	SW	CaCl ₂	Na ₂ CO ₃	0.3	10	0.31	20.00	15.327	0	100
7a(15)	SW	CaCl ₂	Na ₂ CO ₃	0.3	15	0.31	20.00	15.359	-	-
7a(20)	SW	CaCl ₂	Na ₂ CO ₃	0.3	20	0.30	20.00	15.118	-	-
7a(30)	SW	CaCl ₂	Na ₂ CO ₃	0.3	30	0.31	20.00	15.569	-	-
7a(40)	SW	CaCl ₂	Na ₂ CO ₃	0.3	40	0.31	20.00	15.713	-	-
7a(50)	SW	CaCl ₂	Na ₂ CO ₃	0.3	50	0.32	20.00	15.899	-	-

Table A.2. Continued.

Sample ID	Solute	Ca ²⁺ source	CO ₃ ²⁻ source	Total Ca ²⁺ and CO ₃ ²⁻ reactant concentration	Aliquot withdrawal time (minutes)	Precipitate mass (g)	Aliquot volume (ml)	Precipitate mass (mg) per mL aliquot	% vaterite	% calcite
.01(5)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.01	5	0.01	20.00	0.481	33.1	66.9
.01(10)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.01	10	0.02	20.00	0.840	-	-
.01(15)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.01	15	0.02	20.00	0.829	-	-
.01(20)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.01	20	0.16	220.00	0.733	37.5	62.5
.03b(0)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.03	0	0.06	20.00	3.003	26.2	73.8
.03b(5)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.03	5	0.06	20.00	2.770	26.7	73.3
.03b(10)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.03	10	0.05	20.00	2.664	-	-
.03b(15)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.03	15	0.06	20.00	2.832	-	-
.03b(20)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.03	20	0.46	170.00	2.731	14.2	85.8
.06(0)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.06	0	0.07	10.00	7.300	34.1	65.9
.06(5)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.06	5	0.12	20.00	6.150	22.1	77.9
.06(10)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.06	10	0.13	20.00	6.400	-	-
.06(15)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.06	15	0.13	20.00	6.300	-	-
.06(20)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.06	20	0.97	180.00	5.372	12.8	87.2
.1(0)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.1	0	0.12	10.00	12.000	36.7	63.3
.1(2.5)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.1	3	0.20	20.00	10.050	59.3	40.7
.1(5)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.1	5	0.19	20.00	9.600	57.1	42.9
.1(10)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.1	10	0.20	20.00	9.950	-	-
.1(15)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.1	15	1.72	180.00	9.539	-	-

Table A.2. Continued.

Sample ID	Solute	Ca ²⁺ source	CO ₃ ²⁻ source	Total Ca ²⁺ and CO ₃ ²⁻ reactant concentration	Aliquot withdrawal time (minutes)	Precipitate mass (g)	Aliquot volume (ml)	Precipitate mass per mL aliquot	% vaterite	% calcite
.2(5)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.2	5	0.31	20.00	15.650	85	15
.2(10)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.2	10	0.32	20.00	16.000	-	-
.2(15)	NaCl, I=0.7	CaCl ₂	Na ₂ CO ₃	0.2	15	0.32	20.00	15.800	-	-
.2b(0)	NaCl, I=0.5	CaCl ₂	Na ₂ CO ₃	0.2	0	0.23	10.00	22.800	-	-
.2b(2)	NaCl, I=0.5	CaCl ₂	Na ₂ CO ₃	0.2	2	0.40	20.00	19.850	-	-
.2b(5)	NaCl, I=0.5	CaCl ₂	Na ₂ CO ₃	0.2	5	0.40	20.00	19.850	87.4	62.2
.2b(10)	NaCl, I=0.5	CaCl ₂	Na ₂ CO ₃	0.2	10	0.40	20.00	20.200	-	-
.2b(15)	NaCl, I=0.5	CaCl ₂	Na ₂ CO ₃	0.2	15	4.21	180.00	23.361	72.1	27.9
.2d(0)	fsw, I=7	CaCl ₂	Na ₂ CO ₃	0.2	0	0.25	10.00	24.700	-	-
.2d(5)	fsw, I=8	CaCl ₂	Na ₂ CO ₃	0.2	5	0.39	20.00	19.550	87.4	12.6
.2d(10)	fsw, I=9	CaCl ₂	Na ₂ CO ₃	0.2	10	0.39	20.00	19.550	-	-
.2d(3hr40min)	fsw, I=10	CaCl ₂	Na ₂ CO ₃	0.2	220	3.88	200.00	19.400	-	-
.25(0)	fsw, I=.7	CaCl ₂	Na ₂ CO ₃	0.25	0	0.26	10.00	26.100	64	36
.25(2)	fsw, I=.7	CaCl ₂	Na ₂ CO ₃	0.25	2	0.49	20.00	24.500	-	-
.25(5)	fsw, I=.7	CaCl ₂	Na ₂ CO ₃	0.25	5	0.48	20.00	23.800	85.2	14.8
.25(10)	fsw, I=.7	CaCl ₂	Na ₂ CO ₃	0.25	10	0.47	20.00	23.650	-	-
.25(15)	fsw, I=.7	CaCl ₂	Na ₂ CO ₃	0.25	15	4.62	180.00	25.683	-	-

Table A.2. Continued.

Sample ID	Solute	Ca ²⁺ source	CO ₃ ²⁻ source	Total Ca ²⁺ and CO ₃ ²⁻ reactant concentration	Aliquot withdrawal time (minutes)	Precipitate mass (g)	Aliquot volume (ml)	Precipitate mass (mg) per mL aliquot	% vaterite	% calcite
.2c(0)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	0	0.20	10.00	20.000	-	-
.2c(2)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	2	0.39	20.00	19.450	-	-
.2c(5)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	0.37	20.00	18.700	84.9	15.1
.2c(10)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	10	0.37	20.00	18.500	-	-
.2c(15)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	15	3.38	180.00	18.783	79.7	20.3
.25b(0)	MQ	CaCl ₂	Na ₂ CO ₃	0.25	0	0.24	10.00	24.100	-	-
.25b(5)	MQ	CaCl ₂	Na ₂ CO ₃	0.25	5	0.48	20.00	24.150	71.3	28.7
.25b(10)	MQ	CaCl ₂	Na ₂ CO ₃	0.25	10	0.45	20.00	22.550	-	-
.25b(15)	MQ	CaCl ₂	Na ₂ CO ₃	0.25	15	5.63	200.00	28.130	-	-
bc.1(5)	MQ	CaCl ₂	NaHCO ₃	0.1	5	0.67	250.00	2.660	90	10
bc.15(0)	MQ	CaCl ₂	NaHCO ₃	0.15	0	0.03	20.00	1.400	-	-
bc.15(5)	MQ	CaCl ₂	NaHCO ₃	0.15	5	0.08	20.00	3.950	94.2	5.8
bc.15(10)	MQ	CaCl ₂	NaHCO ₃	0.15	10	0.10	20.00	4.750	-	-
bc.15(15)	MQ	CaCl ₂	NaHCO ₃	0.15	15	1.10	190.00	5.789	-	-
bc.2(0)	MQ	CaCl ₂	NaHCO ₃	0.2	0	0.03	20.00	1.650	-	-
bc.2(5)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.15	25.00	6.160	94.5	5.5
bc.2(10)	MQ	CaCl ₂	NaHCO ₃	0.2	10	0.12	18.00	6.722	86.9	13.1
bc.2(15)	MQ	CaCl ₂	NaHCO ₃	0.2	15	1.51	207.00	7.300	-	-

Table A.2. Continued.

Sample ID	Solute	Ca ²⁺ source	CO ₃ ²⁻ source	Total Ca ²⁺ and CO ₃ ²⁻ reactant concentration	Aliquot withdrawal time (minutes)	Precipitate mass (g)	Aliquot volume (ml)	Precipitate mass (mg) per mL aliquot	% vaterite	% calcite
bc.2b(0)	MQ	CaCl ₂	NaHCO ₃	0.2	0	0.04	20.00	2.100	-	-
bc.2b(5)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.36	27.00	13.333	95.8	4.2
bc.2b(10)	MQ	CaCl ₂	NaHCO ₃	0.2	10	0.22	29.00	7.690	-	-
bc.2b(15)	MQ	CaCl ₂	NaHCO ₃	0.2	15	1.40	174.00	8.029	-	-
bc.25(0)	MQ	CaCl ₂	NaHCO ₃	0.25	0	0.07	20.00	3.650	-	-
bc.25(5)	MQ	CaCl ₂	NaHCO ₃	0.25	5	0.19	20.00	9.500	93.8	6.2
bc.25(10)	MQ	CaCl ₂	NaHCO ₃	0.25	10	0.21	20.00	10.400	-	-
bc.25(15)	MQ	CaCl ₂	NaHCO ₃	0.25	15	2.30	190.00	12.084	-	-
bc.3(0)	MQ	CaCl ₂	NaHCO ₃	0.3	0	0.06	10.00	5.800	-	-
bc.3(5)	MQ	CaCl ₂	NaHCO ₃	0.3	5	0.25	20.00	12.400	92.5	7.5
bc.3(10)	MQ	CaCl ₂	NaHCO ₃	0.3	10	0.26	20.00	12.950	-	-
bc.3(15)	MQ	CaCl ₂	NaHCO ₃	0.3	15	2.53	200.00	12.670	-	-
x.2(0)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	0	0.20	10.00	19.600	51.2	48.8
x.2(5)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	0.38	20.00	19.100	77.8	22.2
x.2(10)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	10	0.37	20.00	18.700	77.6	22.4
x.2(15)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	15	3.60	200.00	17.985	63.9	36.1

Table A.2. Continued.

Sample ID	Solute	Ca ²⁺ source	CO ₃ ²⁻ source	Total Ca ²⁺ and CO ₃ ²⁻ reactant concentration	Aliquot withdrawal time (minutes)	Precipitate mass (g)	Aliquot volume (ml)	Precipitate mass (mg) per mL aliquot	% vaterite	% calcite
xbc.2(0)	MQ	CaCl ₂	NaHCO ₃	0.2	0	0.02	10.00	1.600	68.5	31.5
xbc.2(5)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.12	18.00	6.667	93.7	6.3
xbc.2(10)	MQ	CaCl ₂	NaHCO ₃	0.2	10	0.16	20.00	7.900	90.5	9.5
xbc.2(15)	MQ	CaCl ₂	NaHCO ₃	0.2	15	1.60	193.00	8.311	80.2	19.8
Sr-bc-P(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	1.07	150	7.120	76.3	23.7
Sr-bc-P(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	1.06	150	7.040	79.8	20.2
Sr-bc-2x(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.98	150	6.500	75.8	24.2
Sr-bc-2x(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.84	150	5.580	83.5	16.5
Sr-bc-10x(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.82	150	5.447	93.6	6.4
Sr-bc-10x(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.84	150	5.567	85.4	14.6
Sr-c-Pc(1)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	1.36	75	18.080	59.9	40.1
Sr-c-Pc(2)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	1.37	75	18.267	74.4	25.6
Sr-c-2xc(1)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	1.37	75	18.267	72.1	27.9
Sr-c-2xc(2)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	1.37	75	18.267	69.5	30.5
Sr-c-10xc(1)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	1.39	75	18.507	78.6	21.4
Sr-c-10xc(2)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	1.39	75	18.573	-	-

Table A.2. Continued.

Sample ID	Solute	Ca ²⁺ source	CO ₃ ²⁻ source	Total Ca ²⁺ and CO ₃ ²⁻ reactant concentration	Aliquot withdrawal time (minutes)	Precipitate mass (g)	Aliquot volume (ml)	Precipitate mass (mg) per mL aliquot	% vaterite	% calcite
Mg-bc-P(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.79	150	5.260	86.3	13.7
Mg-bc-P(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.79	150	5.247	84.8	15.2
Mg-bc-2x(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.40	150	2.693	66.7	33.3
Mg-bc-2x(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.35	150	2.333	67.5	32.5
Mg-bc-5x(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.20	200	1.020	78.2	21.8
Mg-bc-5x(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.18	200	0.890	0	100
Mn-bc-001c(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	1.02	150	6.820	87.7	12.3
Mn-bc-001c(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.97	150	6.433	90.1	9.9
Mn-bc-01c(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.84	150	5.600	0	n/a*
Mn-bc-01c(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.96	150	6.420	0	n/a*
Mn-bc-05c(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	1.07	150	7.153	0	n/a*
Mn-bc-05c(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.85	150	5.687	0	n/a*
Mn-c-001c(1)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	2.78	150	18.500	82.3	17.7
Mn-c-001c(2)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	2.82	150	18.813	80	20
Mn-c-01c(1)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	2.78	150	18.533	26.2	73.8
Mn-c-01c(2)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	2.85	150	19.007	31.1	68.9
Mn-c-05c(1)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	2.84	150	18.947	0	n/a*
Mn-c-05c(2)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	2.89	150	19.273	14.6	85.4

*Unidentified phase

Table A.2. Continued.

Sample ID	Solute	Ca ²⁺ source	CO ₃ ²⁻ source	Total Ca ²⁺ and CO ₃ ²⁻ reactant concentration	Aliquot withdrawal time (minutes)	Precipitate mass (g)	Aliquot volume (ml)	Precipitate mass (mg) per mL aliquot	% vaterite	% calcite
Fe-bc-001(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	1.01	150	6.740	90.4	9.6
Fe-bc-001(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	1.00	150	6.647	83.8	16.2
Fe-bc-01(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.75	150	4.973	0	100
Fe-bc-01(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.80	150	5.320	0	100
Fe-bc-05(1)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.54	150	3.567	-	-
Fe-bc-05(2)	MQ	CaCl ₂	NaHCO ₃	0.2	5	0.56	150	3.760	0	n/a*
Fe-c-001(1)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	2.84	150	18.953	64.4	35.6
Fe-c-001(2)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	2.84	150	18.947	65.8	34.2
Fe-c-01(1)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	2.81	150	18.713	40.8	59.2
Fe-c-01(2)	MQ	CaCl ₂	Na ₂ CO ₃	0.2	5	2.74	150	18.240	83.9	16.1
org.1c(0)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.1	0	0.11	10	10.500	43.2	56.8
org.1c(5)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.1	5	0.19	20	9.700	84.4	15.6
org.1c(10)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.1	10	1.12	120	9.367	-	-
org.1bc(1)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.1	1	0.00	20	0.150	-	-
org.1bc(5)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.1	5	0.07	20	3.300	98.1	1.9
org.1bc(10)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.1	10	0.40	110	3.664	97.5	2.5
org.2c(0)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.2	0	0.20	10	19.900	72.5	27.5
org.2c(5)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.2	5	0.38	20	18.800	96.7	3.3

Table A.2. Continued.

Sample ID	Solute	Ca ²⁺ source	CO ₃ ²⁻ source	Total Ca ²⁺ and CO ₃ ²⁻ reactant conc.	Aliquot withdrawal time (minutes)	Precipitate mass (g)	Aliquot volume (ml)	Precipitate mass (mg) per mL aliquot	% vaterite	% calcite
org.2c(10)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.2	10	2.37	120	19.733	93.1	6.9
org.2bc(0)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.2	0	0.04	20	2.000	97	3
org.2bc(5)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.2	5	0.16	20	7.750	98.5	1.5
org.2bc(10)	MQ	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.2	10	0.96	110	8.745	98.8	1.2
sworg.1c(0)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.1	0	0.09	5	18.600	9.7	90.3
sworg.1c(5)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.1	5	0.20	20	9.950	10.9	89.1
sworg.1c(10)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.1	10	1.19	125	9.496	7.1	92.9
sworg.1bc(0)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.1	0	0.00	30	0.000	-	-
sworg.1bc(5)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.1	5	0.01	20	0.500	-	-
sworg.1bc(10)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.1	10	0.07	130	0.569	10.1	89.9
sworg.2c(0)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.2	0	0.28	10	28.200	-	-
sworg.2c(5)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.2	5	0.42	20	20.850	72.3	27.7
sworg.2c(10)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	Na ₂ CO ₃	0.2	10	2.43	120	20.275	69.3	30.7
sworg.2bc(0)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.2	0	0.05	20	2.300	93.2	6.8
sworg.2bc(5)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.2	5	0.12	20	6.150	91.5	8.5
sworg.2bc(10)	SW	Ca(CH ₃ COO) ₂ ·H ₂ O	NaHCO ₃	0.2	10	0.89	110	8.082	97.6	2.4

Table A.3. ICP data for trace element doped experiments.

Filtrate						Solid				
Sample ID	Mn ²⁺ ppm	Fe ²⁺ ppm	Mg ²⁺ ppm	Ca ²⁺ ppm	Sr ²⁺ ppm*	Mn ²⁺ ppm	Fe ²⁺ ppm	Mg ²⁺ ppm	Ca ²⁺ ppm	Sr ²⁺ ppm*
<i>NaHCO₃</i>										
Mg-bc-5x(2)L	0.0	0.0	4242.6	5419.6	3.2	0.0	0.0	8.6	256.3	0.1
Mg-bc-5x(1)L	0.0	0.0	5058.6	6248.6	3.2	0.0	0.0	10.3	332.2	0.1
Mg-bc-2x(2)L	0.0	0.0	2592.3	4166.1	1.8	0.0	0.0	5.3	625.4	0.1
Mg-bc-2x(1)L	0.0	0.0	2480.8	4052.8	1.7	0.0	0.0	7.2	557.1	0.1
Mg-bc-P(1)L	0.0	0.0	1541.5	4900.3	1.7	0.0	0.0	4.0	856.9	0.1
Mg-bc-P(2)L	0.0	0.0	1297.6	5741.4	1.7	0.0	0.0	3.0	1005.1	0.1
<i>Na₂CO₃</i>										
Mg-c-Pc(1)	0.0	0.0	813.0	678.0	0.3	0.0	0.0	10.9	271.2	0.0
Mg-c-2xc(1)L	0.0	0.0	1840.9	1121.7	0.6	0.0	0.0	9.1	113.9	0.0
Mg-c-5x(1)	0.0	0.0	4344.0	1951.0	1.5	0.0	0.0	66.1	312.2	0.1
<i>NaHCO₃</i>										
Sr-bc-10x(1)L	0.0	0.0	0.0	965.2	11.9	0.0	0.0	0.0	347.3	0.9
Sr-bc-10x(2)L	0.0	0.0	0.0	184620.0	1662.6	0.0	0.0	0.0	506.4	1.3
Sr-bc-2x(1)L	0.0	0.0	0.0	18049.3	39.3	0.0	0.0	0.0	544.5	0.3
Sr-bc-2x(2)L	0.0	0.0	0.0	20344.6	41.2	0.0	0.0	0.0	1085	0.5
Sr-bc-P(1)L	0.0	0.0	0.0	4608.6	7.4	0.0	0.0	0.0	859.8	0.3
Sr-bc-P(2)L	0.0	0.0	0.0	4914.2	6.5	0.0	0.0	0.0	936.5	0.3
<i>Na₂CO₃</i>										
Sr-c-Pc(1)	0.0	0.0	0.0	14.0	0.3	0.0	0.0	0.5	219.6	0.3
Sr-c-2xc(1)	0.0	0.0	0.0	169.0	3.1	0.0	0.0	0.0	270.9	0.5
Sr-c-2xc(2)	0.0	0.0	0.0	206.0	2.4	0.0	0.0	0.0	235.7	0.4
Sr-c-10xc(1)	0.2	1.0	0.0	140.0	9.9	0.0	0.0	0.0	76.1	0.6
Sr-c-10xc(2)	0.200	0.0	0.0	240.000	17.1	0.0	0.0	0.0	103.1	0.7

* Sr occurred in low concentrations as a contaminant in CO₃ sources; average values were subtracted from Sr experiments.

Table A.3. Continued.

Filtrate						Solid				
Sample ID	Mn ²⁺ ppm	Fe ²⁺ ppm	Mg ²⁺ ppm	Ca ²⁺ ppm	Sr ²⁺ ppm*	Mn ²⁺ ppm	Fe ²⁺ ppm	Mg ²⁺ ppm	Ca ²⁺ ppm	Sr ²⁺ ppm*
<i>NaHCO₃</i>										
Mn-bc-001c(1)L	0.9	0.1	0.0	4307.3	1.4	2.2	0.1	0.4	533.8	0.0
Mn-bc-001c(2)L	1.6	0.1	0.0	4917.7	1.5	1.1	0.0	0.4	241.4	0.0
Mn-bc-01c(1)L	24.1	0.0	0.0	4590.0	1.3	2.4	0.0	0.0	90.1	0.0
Mn-bc-01c(2)L	18.0	0.2	0.0	4744.0	1.4	2.1	0.0	0.0	71.7	0.0
Mn-bc-05c(1)L	114.0	2.3	0.0	5113.2	1.3	2.1	0.0	0.0	15	0.0
Mn-bc-05c(2)L	130.7	0.0	0.0	5284.6	1.6	2.7	0.0	0.0	18.3	0.0
<i>Na₂CO₃</i>										
Mn-c-05c(1)L	1.9	0.0	0.0	454.0	0.3	1.6	0.0	0.0	23.6	0.0
Mn-c-05c(2)L	4.2	0.1	0.0	484.0	0.3	2.3	0.0	0.0	33.8	0.0
Mn-c-01c(1)L	0.2	0.8	0.0	245.0	0.3	1.8	0.0	0.0	135.5	0.0
Mn-c-01c(2)L	0.1	0.1	0.0	139.0	0.2	2.6	0.0	0.0	184.9	0.0
Mn-c-001c(1)L	0.0	0.0	0.0	77.0	0.2	0.7	0.0	0.0	347.4	0.0
Mn-c-001c(2)L	0.2	0.0	0.0	100.0	0.4	0.8	0.1	0.4	373.1	0.0
<i>NaHCO₃</i>										
Fe-bc-001(1)L	0.0	1.3	0.0	4680.0	1.4	0.0	1.1	0.4	674.8	0.0
Fe-bc-001(2)L	0.0	1.3	0.0	5162.4	1.4	0.0	2.0	0.3	1136.6	0.1
Fe-bc-01(1)L	0.0	17.6	0.0	4563.0	1.2	0.0	2.9	0.0	156.8	0.0
Fe-bc-01(2)L	0.0	62.1	0.0	4712.2	1.2	0.0	2.3	0.5	137.3	0.0
Fe-bc-05(1)L	0.3	60.2	0.0	3681.1	0.9	0.0	11.0	0.0	55.1	0.0
Fe-bc-05(2)L	0.0	5.0	0.0	3152.4	0.8	0.0	14.4	0.0	71	0.0
<i>Na₂CO₃</i>										
Fe-c-05(1)L	0.0	10.7	0.0	577.2	0.3	0.0	7.9	0.0	106.4	0.0
Fe-c-01(1)L	0.2	3.0	0.0	190.0	0.4	0.0	3.9	0.0	339.3	0.1
Fe-c-01(2)L	0.0	0.6	0.0	261.0	0.4	0.0	3.7	0.0	325.7	0.1
Fe-c-001(1)L	0.0	0.0	0.0	105.0	0.2	0.0	0.5	0.5	732.2	0.1
Fe-c-001(2)L	0.2	0.0	0.0	176.0	0.4	0.0	0.7	0.4	900.8	0.1

Table A.3. Continued.

Filtrate						Solid							
Sample ID	Trace element milliMol	Ca milliMol	Final te/Ca	Initial te/Ca	Average initial & final te/Ca	Trace element ppm	Ca ppm	te/Ca total	D total (te/Ca)solid / (te/Ca) liquid	D calcite published	% calcite	% vaterite	D vaterite
<i>Fe²⁺</i>													
Fe-bc-001(1)L	0.024	116.766	0.000	0.001	0.001	0.010	8.682	0.001	1.999	3.700	9.6	90.4	1.818
Fe-bc-001(2)L	0.024	128.802	0.000	0.001	0.001	0.011	8.683	0.001	2.134	3.700	16.20	83.8	1.831
Fe-bc-01(1)L	0.315	113.847	0.003	0.010	0.006	0.113	8.542	0.013	2.079	3.700	100.0	0.0	n/a
Fe-bc-01(2)L	1.113	117.569	0.009	0.010	0.010	0.103	8.532	0.012	1.241	3.700	100.0	0.0	n/a
Fe-bc-05(1)L	1.078	91.845	0.012	0.050	0.031	1.039	7.251	0.143	4.640	3.700	100.0	0.0	n/a
Fe-bc-05(2)L	0.090	78.653	0.001	0.050	0.026	1.053	7.232	0.146	5.695	3.700	100.0	0.0	n/a
Fe-c-001(1)L	0.000	2.620	0.000	0.001	0.001	0.005	8.689	0.001	1.058	3.700	35.6	64.4	-0.402
Fe-c-001(2)L	0.000	4.391	0.000	0.001	0.001	0.005	8.691	0.001	1.051	3.700	34.2	65.8	-0.325
Fe-c-01(1)L	0.054	4.741	0.011	0.010	0.011	0.070	8.602	0.008	0.765	3.700	59.2	40.8	-3.493
Fe-c-01(2)L	0.011	6.512	0.002	0.010	0.006	0.070	8.603	0.008	1.392	3.700	16.1	83.9	0.949
Fe-c-05(1)L	0.191	14.401	0.013	0.050	0.032	0.434	8.096	0.054	1.692	3.700	100.0	0.0	n/a
<i>Mg²⁺</i>													
Mg-bc-P(1)L	63.425	122.265	0.519	0.266	0.392	0.067	8.670	0.008	0.020	0.036	13.7	86.3	0.017
Mg-bc-2x(1)L	102.072	101.118	1.009	0.532	0.771	0.184	8.616	0.021	0.028	0.036	33.2	66.7	0.024
Mg-bc-2x(2)L	106.658	103.946	1.026	0.532	0.779	0.121	8.645	0.014	0.018	0.036	32.5	67.5	0.009
Mg-bc-5x(1)L	208.133	155.905	1.335	1.330	1.332	0.435	8.502	0.051	0.038	0.036	21.8	78.2	0.039
Mg-bc-5x(2)L	174.560	135.220	1.291	1.330	1.310	0.470	8.486	0.055	0.042	0.036	100.0	0.0	n/a
Mg-c-Pc(1)	33.450	16.916	1.977	0.266	1.122	0.560	8.445	0.066	0.059	0.049	95.0	0.0	n/a
Mg-c-2xc(1)L	75.742	27.987	2.706	0.532	1.619	1.082	8.210	0.132	0.081	0.049	93.9	0.0	n/a
Mg-c-5x(1)	178.729	48.678	3.672	1.330	2.501	2.635	7.548	0.349	0.140	0.049	100.0	0.0	n/a

Table A.3. Continued.

Filtrate						Solid							
Sample ID	Trace element milliMol	Ca milliMol	Final te/Ca	Initial te/Ca	Average initial & final te/Ca	trace element ppm	Ca ppm	te/Ca total	D total (te/Ca)solid / (te/Ca) liquid	D calcite published	% calcite*	% vaterite	D vaterite
<i>Mn²⁺</i>													
Mn-bc-001c(1)L	0.017	107.468	0.000	0.001	0.001	0.027	8.657	0.003	5.268	15.800	12.3	87.7	3.791
Mn-bc-001c(2)L	0.029	122.697	0.000	0.001	0.001	0.028	8.651	0.003	5.226	15.800	9.9	90.1	4.064
Mn-bc-01c(1)L	0.439	114.521	0.004	0.010	0.007	0.163	8.469	0.019	2.774	15.800	±100	0.0	n/a
Mn-bc-01c(2)L	0.327	118.363	0.003	0.010	0.006	0.183	8.450	0.022	3.389	15.800	±100	0.0	n/a
Mn-bc-05c(1)L	2.076	127.574	0.016	0.050	0.033	0.776	7.627	0.102	3.070	15.800	±100	0.0	n/a
Mn-bc-05c(2)L	2.380	131.852	0.018	0.050	0.034	0.822	7.570	0.109	3.192	15.800	±100	0.0	n/a
Mn-c-001c(1)L	0.000	1.921	0.000	0.001	0.001	0.012	8.684	0.001	2.295	15.800	17.7	82.3	-0.609
Mn-c-001c(2)L	0.004	2.495	0.001	0.001	0.001	0.014	8.672	0.002	1.302	15.800	20.0	80.0	-2.322
Mn-c-01c(1)L	0.004	6.113	0.001	0.010	0.005	0.083	8.584	0.010	1.816	15.800	73.8	26.2	-37.574
Mn-c-01c(2)L	0.002	3.468	0.001	0.010	0.005	0.087	8.581	0.010	1.902	15.800	68.9	31.1	-28.889
Mn-c-05c(1)L	0.034	11.327	0.003	0.050	0.026	0.401	8.145	0.049	1.856	15.800	±100	0.0	n/a
Mn-c-05c(2)L	0.076	12.076	0.006	0.050	0.028	0.404	8.145	0.050	1.759	15.800	85.4	14.6	-80.368
<i>Sr²⁺</i>													
Sr-bc-P(1)L	0.085	114.987	0.001	0.000	0.001	0.001	8.698	0.000	0.241	0.100	23.7	76.3	0.285
Sr-bc-P(2)L	0.074	122.612	0.001	0.000	0.001	0.001	8.698	0.000	0.266	0.100	20.2	79.8	0.308
Sr-bc-2x(1)L	0.449	450.334	0.001	0.001	0.001	0.002	8.695	0.000	0.298	0.100	24.2	75.8	0.361
Sr-bc-2x(2)L	0.470	507.601	0.001	0.001	0.001	0.002	8.696	0.000	0.238	0.100	16.5	83.5	0.265
Sr-bc-10x(1)L	0.136	24.083	0.006	0.005	0.005	0.010	8.679	0.001	0.223	0.100	6.4	93.6	0.232
Sr-bc-10x(2)L	18.975	4606.287	0.004	0.005	0.004	0.010	8.678	0.001	0.273	0.100	14.6	85.4	0.302
Sr-c-Pc(1)	0.003	0.349	0.009	0.000	0.005	0.005	8.674	0.001	0.128	0.100	40.1	59.9	0.147
Sr-c-2xc(2)	0.027	5.140	0.005	0.000	0.003	0.007	8.685	0.001	0.274	0.100	25.6	74.4	0.334
Sr-c-2xc(1)	0.035	4.217	0.008	0.001	0.005	0.007	8.685	0.001	0.180	0.100	27.9	72.1	0.212
Sr-c-10xc(2)	0.195	5.988	0.033	0.005	0.019	0.028	8.638	0.003	0.176	0.100	30.5	69.5	0.209
Sr-c-10xc(1)	0.113	3.493	0.032	0.005	0.018	0.033	8.626	0.004	0.207	0.100	21.4	78.6	0.236

*Some Mn-doped experiments contained no vaterite. Remaining phases consisted of a mixture of calcite and an unidentified phase.

Vita

Emily E. Goodman was born, has lived in many places and will live in many more. She received her BS in Geology from the University of Tennessee at Knoxville in 2005 and will receive her MS in Geology from the same institution in 2007. She will not rest until she has visited every country in the world and tried the national dish. The only foods she really does not care for are cow brains, chicken livers, and peanuts but she will eat them if they are in the national dish. She will try just about anything once and likes to cook, run outdoors, and get down.