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The transformation of aragonite to calcite in the presence of magnesium: Implications for marine diagenesis

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ABSTRACT

Magnesium (Mg) in natural waters plays a critical role in governing carbonate mineral formation, dissolution, and diagenesis. Previous laboratory experiments show that Mg can strongly inhibit direct calcite precipitation as well as aragonite to calcite diagenetic transformation. Data from natural settings, however, suggest that diagenetic calcite in most Phanerozoic limestones has formed in the shallow marine burial realm in the presence of ample Mg. Thus, the diagenetic conditions under which aragonite-rich sediments convert to calcite-rich limestones are poorly understood. Here, we present data from laboratory experiments whereby aragonite is converted to calcite at 70 °C in Mg-bearing solutions to investigate the effects of fluid:solid ratio (F:S), which varies greatly across diagenetic environments, on Mg inhibition and incorporation in calcite. Our data show that not only can the transformation of aragonite to calcite occur in solutions with higher [Mg] than previously shown possible in laboratory experiments, but that progressively lower F:S increase the rate at which aragonite stabilizes to calcite. For example, in experiments with an F:S of 0.3 mL/g, which corresponds to sediments in a closed system with 50% porosity, aragonite stabilizes to calcite in solution with [Mg] = 30 mM (Mg/Ca = 5.14) when an initial high degree of undersaturation with respect to aragonite is used and in a solution with [Mg] = 20 (Mg/Ca = 5.14) when a low degree of undersaturation is used. In contrast, aragonite does not stabilize to calcite after nearly 3000 h in experiments with an F:S of 100 mL/g, which is more typical of an open system, even in a solution with [Mg] = 5 mM (Mg/Ca = 5.14) regardless of the degree of undersaturation. Our results also show that the amount of Mg incorporated into calcite products increases linearly with the increase of F:S. Collectively, these observations further point to F:S as an important factor in carbonate diagenesis with broad implications. First, the observations that transformation of aragonite to calcite is inhibited at high [Mg] and F:S imply that calcite precipitation is unlikely to occur in marine diagenetic environments that are in direct hydrologic contact with seawater. This leaves aragonite dissolution as the dominant diagenetic process in these environments, which may represent an underrated source of alkalinity to the open ocean. Second, transformation from aragonite-rich sediments to the calcite-rich limestones that dominate the rock record is likely promoted by a decrease in the F:S and the development of a closed system during progressive burial.

1. Introduction

Aragonite is the most abundant mineral in modern-day, shallow-marine carbonate sediments (Gischler et al., 2013) and has been for a large proportion of the Phanerozoic Eon (Hashim and Kaczmarek, 2019). Because aragonite is a metastable phase under most Earth surface conditions, aragonitic sediments tend to dissolve during diagenesis, and their dissolution may be accompanied by low-Mg calcite (calcite) precipitation, which is the more stable calcium carbonate polymorph (Morse et al., 2007). Aragonite dissolution and calcite precipitation has been referred to in the literature as transformation, stabilization, transition, conversion, replacement, neomorphism, and recrystallization (Hashim and Kaczmarek, 2019). Here we use the terms stabilization and transformation interchangeably to refer to the coupled reaction of aragonite dissolution and calcite precipitation.

Dissolution of aragonite sediment – and other carbonate minerals – is a significant component of the various oceanic chemical cycles as it increases the buffering capacity of seawater, allowing it to take up more atmospheric CO_2 without a significant change in

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pH (e.g., Morse et al., 2006). Diagenetic stabilization/neomorphism can reset or modify the primary isotopic and trace elemental signatures of carbonate sediments that are routinely used to reconstruct Earth past conditions (e.g., Burdige et al., 2010; Higgins et al., 2018; Wang et al., 2021). Furthermore, stabilization may not necessarily be an isochemical process (Morse et al., 2007), meaning that there could be a net removal or addition of chemical species (e.g., authigenic carbonate precipitation), suggesting that stabilization may play a role in major elemental cycles (e.g., Torres et al., 2020; Turchyn et al., 2021).

Numerous experimental studies have shown that aqueous Mg, the most common divalent cation in seawater, is a strong inhibitor of calcite growth during both direct precipitation of calcite, as well as transformation of aragonite to calcite during diagenesis (Taft, 1967; Bischoff, 1968; Katz, 1973; Berner, 1975; Mucci and Morse, 1983; Davis et al., 2000; Astilleros et al., 2010). It has also been shown that Mg is adsorbed and incorporated in the crystal lattice during calcite precipitation from Mg-bearing solutions, with the amount of Mg incorporated into the growing calcite controlled by various factors, including fluid Mg/Ca ratio, temperature, and precipitation rate (e.g., Mucci and Morse, 1983; Mucci, 1987; Mavromatis et al., 2013; Lammers and Mitnick, 2019). The most commonly cited explanation to the inhibition of calcite growth by Mg is the Cabrera and Vermilyea model (Cabrera and Vermilyea, 1958), which suggests that Mg adsorption on calcite blocks active growth sites (e.g., step edges and kinks), and thus retards the growth rate (e.g., Nielsen et al., 2013). One consequence of this model is that Mg adsorbed at growth sites may be incorporated into the crystal lattice during continued crystal growth (Morse et al., 2007), which in turn produces defects that can destabilize the mineral by increasing its solubility (e.g., Berner, 1975; Davis et al., 2000; De Yoreo and Vekilov, 2003). In this case, inhibition of calcite growth by Mg occurs because of the increase in mineral solubility, and not because Mg is physically blocking surface growth sites.

Previous laboratory studies showed that aragonite to calcite transformation is inhibited, even at low Mg concentrations <5% of modern seawater (Taft, 1967; Bischoff, 1968). This observation initially led to the broad suppositions that aragonite does not stabilize to calcite in seawater (Taft, 1967), or that aragonite must first convert to high-Mg calcite (Bischoff, 1968). However, several subsequent studies examining the buried shallow-marine carbonate sediments of the Great Bahama Bank (GBB) – a major aragonite-dominated bank –reported diagenetic calcite crystals within aragonite-dominated marine sediments at shallow burial depths (<500 m), which were interpreted to have formed via stabilization in seawater-derived pore-fluids (e.g., Melim et al., 1995; Malone et al., 2001; Melim et al., 2002). In some cases, these sediments were/are in contact with pore-fluids whose [Mg] and [Ca] closely resemble seawater (e.g., Malone et al., 2001). Further, geochemical data from Phanerozoic limestones suggest that the vast majority of diagenetic calcite in the rock record have formed in shallow burial from marine derived fluids (e.g., Hasiuk et al., 2016 and references therein). Collectively, these observations suggest that aragonite does stabilize to calcite in the presence of Mg, likely at seawater concentration, despite our inability to experimentally replicate this process in the laboratory (e.g., Taft, 1967; Bischoff, 1968; Katz, 1973; Hashim and Kaczmarek, 2020a).

Most published laboratory studies use experiments whereby calcite is directly precipitated from a supersaturated solution (e.g., Berner, 1975; Mucci and Morse, 1983; Davis et al., 2000; Astilleros et al., 2010; Mavromatis et al., 2013). While these studies have advanced our understanding of the interaction between aqueous Mg and calcite, they are most applicable to calcite forming in open marine settings, but may be less suitable for calcites formed via transformation of aragonite sediments during diagenesis.

Laboratory experiments showing inhibition of calcite growth by Mg during aragonite to calcite transformation (e.g., Taft, 1967; Bischoff, 1968; Hashim and Kaczmarek, 2020a) have traditionally used much higher F:S ratios (fluid-dominated conditions) than are common in the marine burial realm. For example, Taft (1967) used ~0.2 g of aragonite and 40 ml of fluid for most of his stabilization experiments, and Bischoff (1968) used 0.1 g of aragonite and 10 ml of fluid. In the context of early diagenesis, such high F:S ratios may have little geologic relevance. Given that most sediments in the shallow burial realm have porosities of $\leq$70% (e.g., Ehrenberg et al., 2006; Kominz et al., 2011), the F:S ratios used in these experiments do not reflect the conditions where most diagenetic calcite forms in the shallow burial setting. Unlike marine calcite cements, which form in an open system (i.e., fluid-dominated setting), diagenetic calcite has been postulated to form from pore-fluids in low F:S (i.e., sediment-dominated setting) (e.g., Malone et al., 2001; Melim et al., 2002). Accordingly, the primary objective of this study is to experimentally investigate the effect of F:S on Mg inhibition of aragonite to calcite stabilization.

2. Methods

Four series of experiments (Series A-D) were performed whereby aragonite was stabilized to calcite in Mg-bearing solutions. The experiments were conducted to test the effects of fluid:solid ratio (F:S), bulk fluid [Mg], and the saturation state of the initial fluid with respect to (w.r.t.) aragonite. Series A and B used a solution that was slightly undersaturated w.r.t. aragonite ($\Omega_{aragonite} = 0.77$) and in equilibrium w.r.t. calcite ($\Omega_{calcite} = 1$). Series C and D used a solution that was highly undersaturated w.r.t. both aragonite and calcite ($\Omega_{aragonite} = 10^{-6.06}$).

Series A and C include four sub-sets of experiments (A1–A4 and C1–C4) designed to evaluate the effect of F:S. All experiments in Series A and C use the same [Mg], but each set uses a different F:S. Series B and D include three sub-sets of experiments (B1–B3 and D1–D3), which use the same F:S, but different fluid [Mg]. In all experiments, the fluid [Ca] was adjusted so that the initial Mg/Ca molar ratio was = 5.14, which matches average seawater. Experimental conditions for all Series are provided in Table 1. At least one experiment in each of the sets was run in duplicate (supplemental table S1).

Experimental solutions were prepared from deionized MilliQ (18.2 MΩ) water and ACS reagent grade $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$. After preparing the solution at room temperature, the beaker was placed in a constant temperature bath set to $70\,^\circ C \pm 1$. PCO_2 was held constant by bubbling a pre-humidified, commercially purified high-grade nitrogen-CO_2 gas mixture of known composition through the solution. The solution-gas mixtures were allowed to equilibrate for several hours. Solution pH was measured using an Orion® Ross® combination pH electrode connected to a VWR sympHony pH meter. The pH electrode was calibrated at $70\,^\circ C$ using NIST-traceable 4, 7, and 10 buffers. The solution pH was set by adding concentrated HCl or KOH titrants to obtain the desired saturation state (Table 1). The saturation state of the solution w.r.t. aragonite and calcite were determined by calculating the activity coefficient of Ca^{2+} using the Debye-Hückel equation and the activity of ${CO_3}^{2-}$ from the pH-PCO_2 pair and the thermodynamic equilibrium constants for the carbonic acid system (see supplemental Table S1 for detailed calculations). These calculations were confirmed using PHREEQC (Parkhurst and Appelo, 2013) with the LLNL database. PHREEQC was also used for the calculations presented in Fig. 5. In this case, the carbonic acid system was constrained using the alkalinity – PCO_2 pair. Because these calculations were done for a seawater sample, Pitzer database was used due to its suitability for high ionic strength solutions.

Table 1
Summary of experimental conditions[a]

Experiment set	Fluid volume (mL)	Fluid:solid ratio (mL/g)[b]	[Mg] in fluid (mM)	[Ca] in fluid (mM)	n Mg in fluid (μmol)	Initial Ω_{arag}	Initial Ω_{calc}
A-1	15.00	100.0	5	0.97	75.00	0.77	1.00
A-2	0.30	2.2	5	0.97	1.65	0.77	1.00
A-3	0.12	0.8	5	0.97	0.60	0.77	1.00
A-4	0.05	0.3	5	0.97	0.25	0.77	1.00
B-1	0.05	0.3	10	1.95	0.50	0.77	1.00
B-2	0.05	0.3	20	3.88	1.00	0.77	1.00
B-3	0.05	0.3	30	5.83	1.50	0.77	1.00
C-1	15.00	100.0	5	0.97	75.00	8.79E-07	1.15E-06
C-2	0.30	2.2	5	0.97	1.65	8.79E-07	1.15E-06
C-3	0.12	0.8	5	0.97	0.60	8.79E-07	1.15E-06
C-4	0.05	0.3	5	0.97	0.25	8.79E-07	1.15E-06
D-1	0.05	0.3	10	1.95	0.50	8.79E-07	1.15E-06
D-2	0.05	0.3	20	3.88	1.00	8.79E-07	1.15E-06
D-3	0.05	0.3	30	5.83	1.50	8.79E-07	1.15E-06

[a] All experiments use 0.15 g of aragonite a solid reactant, a temperature of 70 °C, and an initial fluid Mg/Ca of 5.14.
[b] Fluid:solid ratios of 0.8 mL/g and 0.3 mL/g correspond to sediments in a closed system with 70% and 50% porosities, respectively (Equation (2)).

All experiments use single crystal aragonite as a solid reactant, which was pulverized using an agate mortar and pestle, sieved to obtain the <63 μm size fraction, and annealed at 200 °C for 4 h to reduce defect-associated strain. Mineralogy of the solid reactant was determined using standard powder x-ray diffraction (XRD) analysis, which confirmed that reactants are >99% aragonite and <1% low-Mg calcite. Elemental composition of the aragonite reactants was confirmed using inductively-coupled plasma mass spectrometry (ICP-MS), which indicate that the aragonite reactants contain 0.71 mg/g Mg and 2.02 mg/g Sr.

The highest F:S (15 mL/0.15 g = 100) in our experiments was intended to represent stabilization/neomorphism in a fluid-dominated setting (e.g., sediment-water interface). The lowest F:S ratio (0.05 mL/0.15 g = 0.3), in contrast, was intended to represent stabilization in a closed system of sediments with 50% porosity. Although a porosity of 50% is more typical of mud-dominated carbonate sediments in shallow burial settings (e.g., Kominz et al., 2011), and that coarse grained sediments are generally less porous (e.g., Ehrenberg et al., 2006), using a F:S ratio lower than 0.3 mL/g was technically challenging. Preliminary experiments with F:S of 0.18 mL/g (i.e., porosity = 35%) showed that the very small fluid volume did not completely mix with the solid reactant likely due to surface tension and aragonite hydrophobicity. Accordingly, the lowest F:S used was 0.3 mL/g, which was calculated using the following equation assuming an aragonite density of 2.93 $g\,cm^{-3}$:

$$\frac{\text{fluid}}{\text{solid}} = \frac{\text{porosity}}{(1-\text{porosity}) * \text{density}} \tag{1}$$

All stabilization experiments were performed in Teflon-lined stainless steel acid digestion vessels charged with solid and fluid reactants. Sealed reaction vessels were placed into a pre-heated convection oven set to 70 °C for predetermined times based on previous work by Hashim and Kaczmarek (2020b). Upon removal from the oven, reaction vessels were immediately cooled to room temperature using forced air. Solid and fluid contents were then separated using a vacuum flask. Solid contents were rinsed in DI water and dried in a vacuum desiccator. Fluids were centrifuged multiple times and stored in plastic vials for elemental analyses.

Standard powder XRD techniques were used to determine the mineralogy of solids following the methods described in Hashim and Kaczmarek (2020a). Percent calcite in experimental products was calculated using the intensities of aragonite 111 peak and calcite 104 peak. Scanning electron microscope (SEM) imaging was performed on a JEOL 7500F using an accelerating voltage of 20 kV and a working distance of 10 mm. Samples were coated with a 10 nm of osmium to reduce the charging effect.

Table 2
Avrami rate equation constants (Eq. (2)) for reaction curves shown in Fig. 2

Experimental set	*A*	*k*	*n*
A-4	98	2.90E-07	2.71
B-1	99	3.67E-08	2.63
B-2	99	1.91E-08	2.65
C-2	99	1.00E-08	3.00
C-3	99	3.50E-10	4.00
C-4	98	5.00E-08	3.18
D-1	96	5.74E-10	3.32
D-2	90	1.50E-08	2.70
D-3	95	3.30E-10	3.15

[Ca], [Mg], and [Sr] in the fluids, [Ca] and [Mg] in solid products, and [Sr] in solid reactants were measured on a Thermo Scientific Quadrupole-ICP-MS (iCAP Q) equipped with an Elemental Scientific PrepFAST 2 Automation System. Solids were dissolved in 2% HNO_3 (w/v) (Optima grade). All samples were measured against matrix-matched standards. Sensitivity drift was corrected for with standard-sample bracketing methods.

3. Results

Mineralogical and geochemical data are compiled in supplemental table S1. In all cases, and consistent with previous studies (e.g., Katz, 1973), aragonite reactants stabilize to calcite polyhedral microcrystals (Fig. 1). Plots of percent calcite versus reaction time for all experiments are shown in Fig. 2. Reaction curves are fitted to the experimental data using a modified version of Avrami equation (Avrami, 1939):

$$y = A(1 - e^{-kx^n}) \tag{2}$$

where y = calcite product (%), x = reaction time (hours), and A, k, and n are constants that are given in Table 2. The constant n is characteristic of the nucleation and growth processes, k is the Avrami kinetic constant (Avrami, 1939), and A is a scaling factor to convert y values to percent.

Results from Series A show that calcite products formed in detectable amounts in the lowest F:S experiments of 0.3 mL/g (Experiment A-4). In contrast, no calcite products were detected in experiments conducted at higher F:S (Experiments A-1, A-2, and A-3) after 3018 h for Experiment A-1 and 1560 h for Experiments A-2 and A-3 (Fig. 2a). Results from Series B show that calcite formed in experiments using fluid [Mg] = 10 mM and 20 mM (Experiments B-1 and B-2) but not in fluid [Mg] = 30 mM (Experiment B-3). Further, the overall reaction rate and the induction period (the period during which no products are observed) correlate negatively with fluid [Mg] (Fig. 2b).

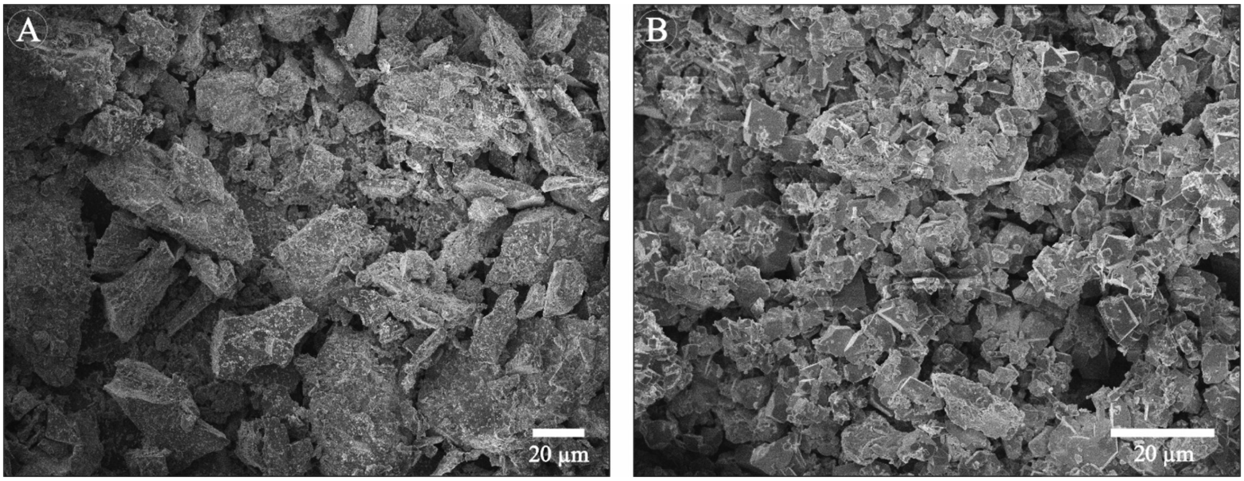

Fig. 1. (A) SEM image of the pulverized, sieved, and annealed single crystal aragonite used as a reactant in all experiments. (B) SEM image of calcite polyhedral microcrystals that resulted from the stabilization of aragonite. This image is for calcite from experiment B-1-5, which used a solution with [Mg] = 10 mM, [Ca] = 1.95 mM, fluid to solid ratio = 0.3 mL/g, and a reaction time = 815 hours.

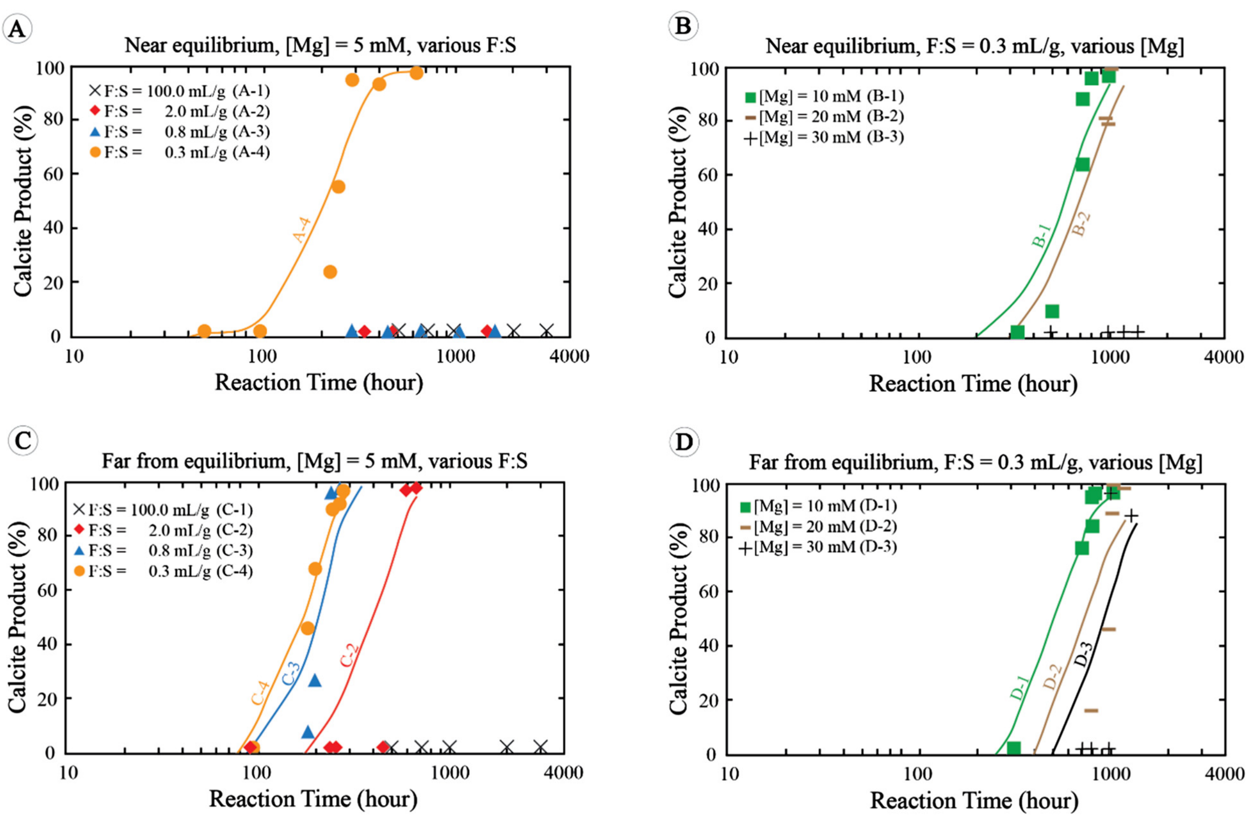

Fig. 2. Plots of reaction time versus percent calcite products for all experiments. Reaction curves were fitted to the data using Avrami equation (Eq. (2)). Plot A presents data from Experimental Series A which used a low degree of undersaturation with respect to aragonite, [Mg] = 5 mM, and various fluid to solid ratios (F:S). The reaction curve was fitted to Experiment A-4 because it was the only Experiment in Series A that produced calcite. Plot B presents data from Experimental Series B, which used a low degree of undersaturation, F:S of 0.3 mL (representative of sediments with 50% porosity in a closed system), and various [Mg]. Plot C presents data from Series C, which used a high degree of undersaturation, [Mg] = 5 mM, and various F:S. Plot D presents data from Experimental Series D, which used a high degree of undersaturation, F:S of 0.3 mL, and various [Mg]. In all experiments, the initial fluid Mg/Ca ratio is 5.14.

Results from experimental Series C show that calcite products formed in experiments that use F:S $\leq$2 mL/g (Experiments C-2, C-3, and C-4). In these experiments, the overall reaction rate exhibits a negative correlation with F:S (Fig. 2c). In contrast, no calcite was detected in experiments that use F:S of 100 mL/g after 2996 h (Experiment C-1). Results from experimental Series D show that the overall aragonite to calcite reaction rate correlates negatively with fluid [Mg] (Fig. 2d). For example, aragonite stabilizes to >80% calcite after ~720 h in fluid [Mg] = 10 mM (Experiment D-1) but it takes 1300 h for aragonite to stabilize to > 80% calcite in fluid [Mg] = 30 (Experiment D-3).

Elemental data from Experiment C-2 show a decrease in fluid [Mg] and an increase in [Sr] with reaction time (Fig. 3). Fluid [Ca] initially increases with reaction time then decreases prior to calcite formation (Fig. 3). All calcites produced in Experiment C and Experiment A-1 contain Mg, the amount of which is proportional

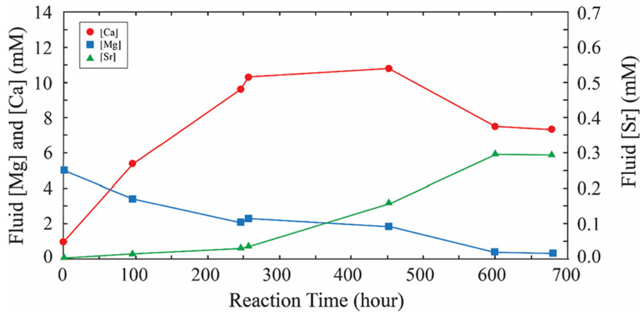

Fig. 3. Cross plot showing the evolution of fluid [Ca], [Mg], and [Sr] during the aragonite to calcite stabilization reaction for Experiment C-2 (high degree of undersaturation, [Mg] = 5 mM and fluid:solid ratio = 2 mL/g). Experiment C-2 is characterized by an induction period of ~600 hours during which no calcite forms (Fig. 2C). This plot shows that, during the induction period, [Mg] decreases, [Sr] increases, and [Ca] increases during the first 450 hours then decreases prior to the formation of calcite. Following calcite formation, [Ca], [Mg], and [Ca] remain nearly constant.

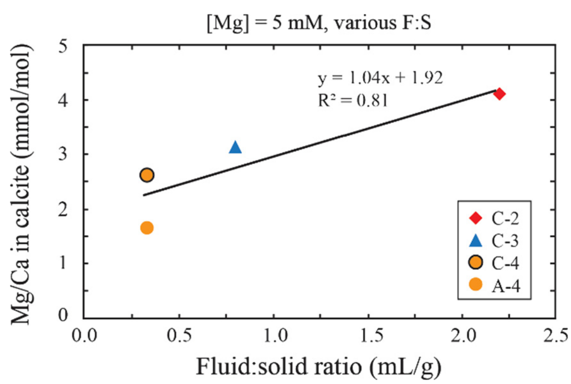

Fig. 4. Cross plot showing an increase in Mg/Ca in calcite products with the increase in fluid:solid ratio. All experiments in this figure used an initial fluid with [Mg] = 5 mM and Mg/Ca = 5.14.

to F:S (Fig. 4). More specifically, higher F:S ratios correlate with higher Mg/Ca in the calcite products (Fig. 4).

4. Discussion

The following discussion hinges on four key observations regarding the role of fluid:solid (F:S) on aragonite to calcite stabilization/neomorphism, which are summarized here. Specifically, lower F:S ratios are observed to: (i) permit stabilization at 70 °C from aragonite to low-Mg calcite (calcite) in Mg-bearing fluids (Fig. 2a), (ii) increase the overall rate of aragonite to calcite transformation (Fig. 2c), (iii) permit stabilization in fluids with higher [Mg] than have been previously shown possible (Figs. 2b and 2d), and (iv) decrease the amount of Mg incorporated in calcite (Fig. 4).

4.1. The effect of F:S on Mg inhibition of stabilization

Stabilization involves two general reactions: aragonite dissolution and calcite precipitation. Aqueous Mg does not interfere with aragonite dissolution (Morse et al., 2007), but it has long been documented to have a strong retarding effect on calcite nucleation and growth (e.g., Taft, 1967; Berner, 1975; Mucci and Morse, 1983; Davis et al., 2000; Mavromatis et al., 2013). Our results show that all experiments that ultimately produced calcite are characterized by an initial induction period during which no calcite forms in a detectable amount (Fig. 2). The duration of the induction period shortens with the decrease of fluid [Mg] (Figs. 2b and 2) and with the decrease of the F:S (Figs. 2a and 2c). That is, calcite takes less time to form when fluid [Mg] and F:S are lower. The induction period has been suggested to represent the period during which aragonite dissolves and calcite nucleates (Bischoff, 1968). What lengthens the induction period is likely the adsorption of Mg on calcite nuclei, which has been suggested by numerous authors to block active growth sites or destabilizes calcite by increasing its solubility (Davis et al., 2000; Morse et al., 2007; Nielsen et al., 2013). This interpretation is consistent with previous studies (e.g., Taft, 1967; Bischoff, 1968) and is supported by the observation that during the induction period, fluid [Mg] decreases with reaction time (Fig. 3), likely due to Mg adsorption and incorporation into calcite (Fig. 4), resulting in subsequent stabilization occurring in a solution depleted in Mg.

To better understand the role of Mg during stabilization, a closer look at this coupled reaction is required. The reaction in our experiments is envisioned to start off with the dissolution of some of the aragonite reactant, the amount of which depends on the initial degree of undersaturation (Section 4.2). Aragonite dissolution is evidenced by the increase in fluid [Ca] and [Sr] with reaction time (Fig. 3). Aragonite dissolution continues until equilibrium w.r.t. aragonite is reached, at which point the solution is also supersaturated w.r.t. calcite because calcite is less soluble than aragonite (Morse et al., 2007). Consequently, calcite begins to nucleate and grow while adsorbing Mg from the solution until the solution is saturated w.r.t. calcite. Because a solution that is saturated w.r.t. calcite is also undersaturated w.r.t. aragonite, precipitation of calcite would result in further dissolution of aragonite. This coupled aragonite dissolution and calcite precipitation continues until all the aragonite reactant is consumed. If Mg is present in small concentrations, it can be adsorbed and incorporated into calcite, which leads to its partial or complete removal from the solution as observed in Experiment C-2 (Fig. 3), thus the stabilization reaction can continue. Given that only a small amount of Mg is incorporated into calcite, the resultant calcite would still be low-Mg calcite (i.e., contains <4 mol% $MgCO_3$) with similar or even lower solubility than pure calcite (Morse et al., 2007). In the case of high fluid [Mg], however, the initial adsorption and incorporation of Mg into calcite does not significantly remove Mg from the solution. In this case, the remaining high fluid [Mg] can retard the overall reaction by inhibiting calcite growth, which may explain why experiments with higher fluid [Mg] exhibited slower reaction rates or produced no calcite at all (Figs. 2b and 2d).

Whereas it is relatively straightforward to explain the effect of fluid [Mg] on the inhibition of aragonite to calcite stabilization, the observation that lower F:S enables stabilization and corresponds to faster reaction rates (Figs. 2a and 2c) requires further elucidation. The fact that stabilization is a coupled dissolution – precipitation reaction means that the chemical ingredients required for calcite growth (i.e., Ca^{2+} and $CO_3{}^{2-}$) are supplied by the dissolving aragonite. Ideally, in a pure solution that is devoid of any chemical inhibitors, F:S is not expected to exert an effect on the reaction other than a possible impact on the diffusion of the various chemical species (Hashim and Kaczmarek, 2020a). Yet, in the presence of a kinetic inhibitor such as Mg, higher fluid volumes mean that the amount of Mg would be higher because total number of moles of Mg is determined not only by its concentration but also by fluid volume. Thus, decreasing the fluid volume, which lowers the F:S, has the same effect on the total amount of Mg in the solution as lowering Mg concentration. In both cases, a smaller amount of Mg can be more effectively pulled out of the solution by being incorporated into calcite (Section 4.3).

The hypothesis that stabilization is inhibited by total available aqueous Mg and not Mg concentration better explains our observations that induction period duration decreases, and the overall reaction rate increases with the decrease of [Mg] and F:S (Fig. 2). More specifically, aragonite reactants in Experiments A-1 and C-1 did not stabilize to calcite despite low fluid [Mg] (5 mM), likely because of the high F:S, which leads to a relatively high amount of Mg (75 μmol) (Figs. 2a and 2c). In contrast, aragonite reactants in Experiments B-1, B-2, D-1, D-2, and D-3 stabilized to calcite despite fluid [Mg] being higher than Experiments A-1 and C-1 (10 mM in B-1 and D-1, 20 mM in B-2 and D-2, and 30 mM in D-3), likely because of the low F:S, which leads to relatively small Mg amounts (0.50, 1.00, and 1.50 μmol, respectively) (Table 1; Fig. 2).

One implication of this line of reasoning is that mineralogical stabilization of metastable carbonates in marine-derived pore-fluids may be promoted by a decrease in the F:S during burial. It is well known that sediments become increasingly compacted and gradually lose porosity with depth (e.g., Ehrenberg et al., 2006; Kominz et al., 2011), which necessarily causes a decrease in the F:S. This means that as burial increases, the sediments are in contact with less fluid and thus less total available Mg in pore fluids, which perhaps allows aragonite dissolution to be accompanied by calcite precipitation from pore-fluids with high [Mg]. Increased burial also hydrologically isolates sediments from seawater – the vast source of Mg – effectively preventing pore-fluid Mg from being replenished as it decreases due to its incorporation into the growing calcite.

4.2. The role of the saturation state

Although our experiments exhibit similar trends regarding the effect of F:S on stabilization/neomorphism regardless of the initial saturation state (Fig. 2), two major differences are noted: (i) stabilization in the far from equilibrium experiments occurred in the [Mg] = 30 mM solution but not in the near equilibrium experiments with the same fluid [Mg], and (ii) in equivalent experiments, the far from equilibrium experiments exhibited overall faster stabilization rates than the near equilibrium experiments (Fig. 2). To explain these observations, the effect of the initial saturation state on the stabilization reaction is considered. As discussed in Section 4.1, the stabilization reaction starts with aragonite dissolution, and the amount of aragonite that dissolves is determined by the degree of undersaturation. Higher initial degree of undersaturation permits more aragonite to dissolve before equilibrium w.r.t. aragonite is attained. The dissolving aragonite releases Ca^{2+} into the solution which necessarily decreases the Mg/Ca ratio. Accordingly, when the starting fluids are more undersaturated w.r.t. aragonite, more aragonite is dissolved, and thus Mg/Ca ratio would be lower in the fluid from which calcite precipitates. This could explain the observed differences between experiments conducted at high and low degrees of undersaturation (Fig. 2) since a low Mg/Ca ratio permits stabilization even if [Mg] is high (Section 4.3). To further explore the effect of the initial saturation state on solution chemistry, we calculated the fluid Mg/Ca ratio when equilibrium w.r.t. aragonite is reached after aragonite dissolution as a function of the initial degree of undersaturation. These calculations were performed for a solution of average seawater composition with initial Mg/Ca = 5.14 at 25 °C and 1 bar (Fig. 5). The calculations show that a large degree of undersaturation is required to produce a substantial decrease in the Mg/Ca ratio. For example, if the initial $\Omega_{aragonite}$ is 0.1, the Mg/Ca ratio when the solution is in equilibrium with aragonite ($\Omega_{aragonite}$ is 1) would decrease from 5.14 to 4.97, or by 3%, and if $\Omega_{aragonite}$ is 0.001, Mg/Ca would decrease to 4.51, or by 12% (Fig. 5).

It should be noted that, in diagenetic environments, several redox reactions within sediments, including oxidation of organic matter and sulfide and reduction of sulfate (Morse et al., 1985; Walter and Burton, 1990; Sanders, 2003; Morse et al., 2007; Present et al., 2021), can continuously release CO_2 into pore-fluids, which decreases the solution pH and thus the saturation state. This implies that pore-fluids may not be highly undersaturated at any given time, yet the continuous release of CO_2 could maintain pore-fluid undersaturation and thus causes significant aragonite dissolution and substantial decrease in Mg/Ca ratio. Accordingly, while the initial degree of undersaturation is important, the amount of acid produced over time is more important in dictating how much aragonite is dissolved. It is therefore more accurate to say that a high degree of undersaturation or a relatively large volume of acid release is required to cause significant aragonite dissolution and substantial decrease in Mg/Ca ratio.

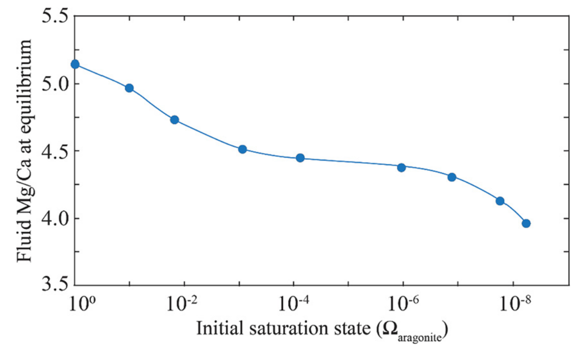

Fig. 5. Model of Mg/Ca ratio in a seawater solution at equilibrium with aragonite as a function of aragonite initial saturation state. The calculations were performed for a seawater sample with initial Mg/Ca ratio of 5.14 at 25 °C and 1 bar. For an example of how to read this graph, the dissolution of aragonite in a seawater sample with a saturation state ($\Omega_{aragonite}$) of 0.01 would decrease the Mg/Ca ratio from 5.14 to ∼4.7 when the solution is at equilibrium with aragonite ($\Omega_{aragonite} = 1$).

4.3. Evolution of fluid Mg/Ca during stabilization

It has been shown that stabilization/neomorphism of aragonite to calcite and direct precipitation of calcite may occur even when [Mg] is high, given that Mg/Ca ratio is low (Katz, 1973; Morse et al., 1997). Katz (1973), for example, stabilized aragonite to calcite at 25 °C in a solution containing [Mg] = 40 mM and [Ca] = 100 mM (Mg/Ca = 0.4). Based on this observation, Katz (1973) postulated that a decrease in the Mg/Ca ratio is required for stabilization to occur in marine diagenetic environments, and further speculated that this would happen via aragonite dissolution through *in situ* production of acid, which would increase fluid [Ca]. Subsequent studies have indeed shown that pore-fluid [Ca] can increase with depth, causing a decrease in Mg/Ca ratio (Eberli et al., 1997; Swart, 2015 and references therein). Some of our data support the hypothesis that aragonite dissolution can increase fluid [Ca] and thus significantly decrease Mg/Ca ratio prior to calcite formation (Fig. 3). The increase in fluid [Sr] with reaction time further supports the occurrence of aragonite dissolution (Fig. 3). However, it is important to emphasize that a significant increase in fluid [Ca], and the accompanied decrease in Mg/Ca ratio, as a result of aragonite dissolution is expected only when the initial degree of undersaturation is high, such as in experiment C-2 shown in Fig. 3, or when a large volume of acid is added (Section 4.2). When the degree of undersaturation is low, aragonite dissolution is incapable of decreasing Mg/Ca ratio considerably (Fig. 5).

While it is established that aragonite dissolution can effectively decrease Mg/Ca ratio, an important question arises: Is the decrease in fluid Mg/Ca ratio a prerequisite for aragonite to calcite stabilization in marine diagenetic environments? Malone et al. (2001) observed diagenetic calcite in the subsurface of the slope of the GBB over a depth interval where the pore-fluid [Ca] and [Mg] – and thus Mg/Ca – are similar to modern seawater. They further reported that the appearance of diagenetic calcite is coincident with a gradual decrease in pore-fluid [Mg], though no significant increase in pore-fluid [Ca] was observed. Collectively, these observations, and those presented in the current study, suggest that a

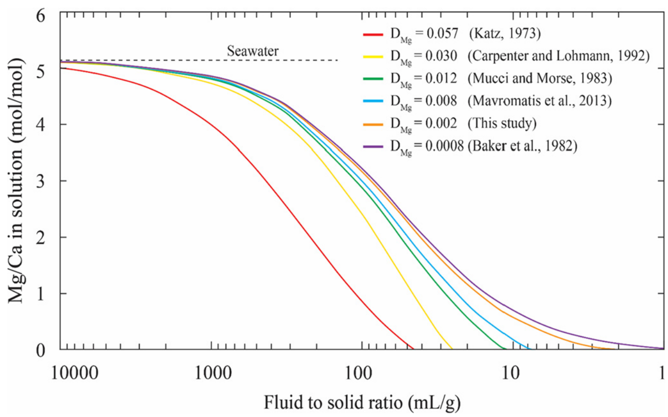

Fig. 6. The modeled decrease in fluid Mg/Ca ratio during aragonite to calcite stabilization as a function of fluid to solid ratio (F:S) for different Mg partition coefficients (D_{Mg}). The calculations used an initial Mg/Ca ratio of 5.14 and assumed a closed system. See supplemental materials for more details regarding calculations and partition coefficients. The fluid Mg/Ca ratio decreases as a result of stabilization because Mg is removed from the solution due to its incorporation into calcite while Ca required for calcite growth is provided by aragonite. The decrease is more prominent at low F:S because there is less amount of Mg in the solution when the fluid volume is small. For an example of how to read this graph, if fluid to solid ratio is 100 mL/g, stabilization of aragonite to calcite would decrease the fluid Mg/Ca ratio from 5.14 to ∼3 if the D_{Mg} of Mucci and Morse (1983) is used.

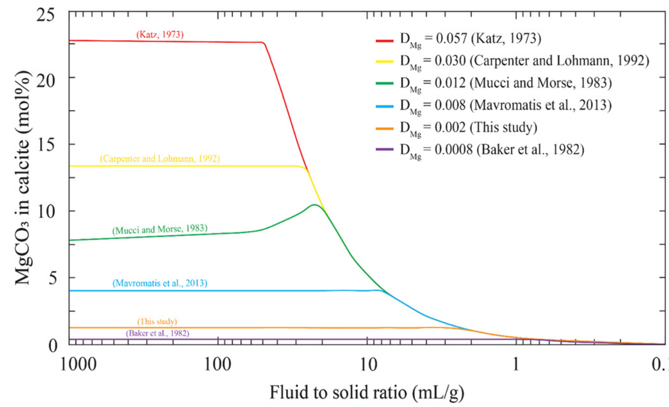

Fig. 7. The modeled Mol% $MgCO_3$ incorporated into calcite stabilized from aragonite in a closed system for different Mg partition coefficients (D_{Mg}) plotted as a function of fluid to solid ratio (F:S). When F:S is high, $MgCO_3$ in calcite is controlled by D_{Mg}. As F:S decreases, the amount of Mg in the fluid becomes insufficient to satisfy the amount of Mg required by the D_{Mg} which leads to the decline of $MgCO_3$ in calcite. Note that below a F:S of 7 mL/g, a calcite with <4 mol% $MgCO_3$ (low-Mg calcite) would precipitate regardless of D_{Mg}. See supplemental materials for calculation details. The increase in $MgCO_3$ with the decrease of F:S for the curve of Mucci and Morse (1983) is also discussed in supplemental materials.

decrease in Mg/Ca ratio prior to stabilization is not required. Instead, we propose here that the process of stabilization in low F:S settings and a closed system is capable of decreasing the fluid Mg/Ca ratio via adsorption and incorporation of Mg into calcite. This may represent an alternative mechanism by which stabilization occurs in case little or no aragonite dissolution takes place to decrease Mg/Ca ratio significantly.

The above hypothesis is supported by results showing that fluid [Mg] decreases before calcite forms in any detectable quantities (Fig. 3). This decrease in [Mg] is most likely associated with Mg adsorption on calcite nuclei and its subsequent incorporation during continued crystal growth (Fig. 4). Interestingly, incorporation of Mg from the fluid during crystal growth can significantly decrease Mg/Ca ratios only when fluid volume is small (i.e., low F:S). For example, in 1 L of seawater, the removal of 3 mmol of Mg from the fluid will change the fluid Mg/Ca ratio from 5.14 to 4.85, or by only 6%. In contrast, in 0.1 L of seawater, the removal of 3 mmol Mg will change the Mg/Ca ratio of the fluid from 5.14 to 0.22, or by 96%. Given that the amount of Mg incorporated into calcite is determined by Mg partition coefficient (D_{Mg}), the decrease in fluid Mg/Ca ratio due to Mg incorporation into calcite can be calculated as a function of F:S ratio. Assuming a closed system and a pore-fluid in near equilibrium with aragonite and with Mg/Ca ratio of 5.14, the evolution of fluid Mg/Ca ratio as a function of F:S for several D_{Mg} is presented in Fig. 6 (see supplemental materials regarding calculations). Unsurprisingly, the calculations show that higher D_{Mg} correspond to a greater decrease in fluid Mg/Ca ratio as F:S decreases (Fig. 6). They also show that when the F:S is high (>1000 mL/g), fluid Mg/Ca ratio does not decrease below 4 regardless of D_{Mg} (Fig. 6). In contrast, when F:S is low (<30 mL/g), fluid Mg/Ca ratio drops substantially even for the smallest $D_{Mg} = 0.0008$ of Baker et al. (1982). These calculations illustrate that in low F:S scenarios, the process of stabilization is capable of decreasing fluid M/Ca ratio considerably even when D_{Mg} is small. How low F:S needs to be for a given decrease in fluid Mg/Ca ratio depends on D_{Mg}.

It is also possible to calculate the amount of Mg incorporated into calcite during stabilization/neomorphism in a closed system as a function of F:S (Fig. 7; see supplemental materials regarding calculations). It is observed that the calcite mol% $MgCO_3$ is dictated by the D_{Mg} when F:S is high (Fig. 7). As F:S decreases, however, less Mg is incorporated into calcite than predicted by D_{Mg} because there is not enough Mg in the solution to satisfy the amount of Mg predicted by the D_{Mg}. The exact F:S below which Mg in solution becomes insufficient to produce calcite with the amount of Mg predicted by D_{Mg} is directly proportion to D_{Mg}. Importantly, the calculations in Fig. 7 predict that calcite with <4 mol% $MgCO_3$ (low-Mg calcite) would precipitate from a solution with initial Mg/Ca ratio of 5.14 given that the F:S is <7 mL/g regardless of D_{Mg}. These predictions are consistent with our experimental data, which demonstrate that the Mg/Ca in calcite is proportional to the F:S (Fig. 4). That is, the amount of Mg incorporated into calcite increases with the increase of the F:S despite initial [Mg] and Mg/Ca ratio being the same.

4.4. Implications for marine diagenesis

Given that aragonite is metastable under Earth surface conditions (Morse et al., 2007), dissolution of aragonite sediments is a common process in meteoric, mixing, and marine diagenetic environments (Morse et al., 1985; Melim et al., 1995, 2002; Sanders, 2003; James et al., 2005; Cherns and Wright, 2009; Present et al., 2021). In marine diagenetic environments, dissolution is driven by pore-fluid undersaturation with respect to (w.r.t.) aragonite which has been commonly attributed to organic matter and sulfide oxidation and sulfate reduction (Morse et al., 1985; Walter and Burton, 1990; Present et al., 2021). A key question is whether aragonite dissolution would be accompanied by calcite precipitation.

If pore-fluids are supersaturated w.r.t. calcite, aragonite dissolution would potentially be followed by calcite precipitation. In marine environments, the precipitating calcite would incorporate Mg, the amount of which (mol% $MgCO_3$) depends on several factors including fluid Mg/Ca ratio, fluid:solid ratio (F:S), temperature, and precipitation rate (e.g., Fig. 4; Katz, 1973; Mucci and Morse, 1983; Mavromatis et al., 2013; Lammers and Mitnick, 2019). Most experimental studies show that, at 25 °C, a solution with a modern seawater Mg/Ca ratio of 5.14 would precipitate calcite with $MgCO_3$ of ∼8 mol% (Morse et al., 2006; and references therein). Furthermore, marine calcite that precipitates presumably inorganically in shallow water depths in tropical and subtropical regions typically contains ∼12 mol% $MgCO_3$ (Hover et al., 2001; Morse et al., 2006, 2007; Burdige et al., 2010). Based on these observations, low-Mg calcite (calcite) is unlikely to precipitate in diagenetic environments that are in hydrological contact with seawater where Mg/Ca ratio is relatively high. If pore-fluids are only slightly supersaturated w.r.t. calcite, HMC is also unlikely to precipitate because HMC solubility increases with Mg content (Morse et al., 2006), making pore-fluids undersaturated or, at best, in equilibrium w.r.t. most HMC phases. Even if it precipitates, HMC is fated to dissolve because it is, like aragonite, a metastable phase. Accordingly, the inhibitory effect of Mg represents one of the major kinetic reasons that limit calcite precipitation in marine diagenetic environments, in addition to other factors (e.g., Turchyn et al., 2021). This leaves aragonite dissolution as the dominant process in the marine diagenetic environment that is hydrologically open to seawater. Data and calculations from the present study suggest that aragonite dissolution accompanied by low-Mg calcite precipitation (i.e., stabilization) is promoted by a decrease in the F:S and the development of a closed system. Such conditions occur naturally during burial, which leads to lower porosity (Ehrenberg et al., 2006; Kominz et al., 2011) and thus lower F:S as well as hydrologic isolation from seawater (Swart, 2015). Thus, we hypothesize that, aragonite dissolution is the dominant process in the fluid buffered interval in marine diagenetic environments whereas aragonite to calcite stabilization is the dominant process in the sediment buffered interval. This hypothesis is consistent with the observations of Melim et al. (2002) who identified two styles of marine-burial diagenesis in the GBB and its margin: open system characterized by aragonite dissolution with no significant calcite precipitation and closed system characterized by aragonite dissolution and calcite precipitation (i.e., stabilization).

The above hypothesis has several implications. First, it provides an explanation for the proposition that the vast majority of diagenetic low-Mg calcite in Phanerozoic limestones has stabilized from aragonite in marine diagenetic environments (e.g., Kaczmarek et al., 2015; Hasiuk et al., 2016; Hashim and Kaczmarek, 2019 and references therein). One of the key aspects of the hypothesis is that no special conditions are required for stabilization to occur in seawater-derived pore-fluids other than the natural burial of sediments. Second, our hypothesis has significant implications for models that attempt to quantify the diagenetic impact on the geochemical signatures of marine carbonates (e.g., Ahm et al., 2018; Higgins et al., 2018; Wang et al., 2021). In general, most models assume that stabilization/neomorphism of aragonite to calcite in marine diagenetic environments takes place in both fluid-buffered and sediment-buffered intervals, which may not necessarily be the case based on our findings. Third, the proposition that aragonite dissolution is the dominant process in the diagenetic interval that is hydrologically open to seawater implies that aragonite dissolution could be a significant source of alkalinity to the ocean (Burdige et al., 2010) since aqueous Ca^{2+} and HCO_3^- are less likely to re-precipitate as calcite. The magnitude of contribution from aragonite dissolution to the alkalinity cycle is dependent on the extent of the acid-producing processes that promote and maintain pore-fluid undersaturation w.r.t. aragonite (Morse et al., 1985; Walter and Burton, 1990) as well as advection and diffusion rates within sediments which carry aqueous species (Ca^{2+} and HCO_3^-) to the ocean. Lastly, the hypothesis provides an explanation to previous suggestions that sedimentation/accumulation rates reflect diagenetic loss of aragonite in addition to primary productivity (Sanders, 2003), and that a significant proportion of aragonite sediments is recycled back to the ocean and does not make it to the rock record (James et al., 2005). The proportion of aragonite that dissolves versus stabilizes to calcite is yet to be estimated.

4.5. The applicability of experiments to natural settings

Laboratory investigations of carbonate mineral kinetics often focus on one process (e.g., dissolution or precipitation) and one mineral (e.g., Berner, 1975; Mucci and Morse, 1983; Davis et al., 2000; Astilleros et al., 2010; Mavromatis et al., 2013). Studying the effect of fluid:solid ratio (F:S) in the context of carbonate diagenesis, however, requires considering both aragonite dissolution and calcite precipitation concurrently (i.e., stabilization) as we have done here. While most studies typically employ a relatively high degree of disequilibrium so that reaction kinetics are fast enough to be studied in a reasonable period of time since reaction kinetics generally increase with distance from equilibrium (Morse et al., 2007; Hashim and Kaczmarek, 2021), this cannot be done for aragonite to calcite stabilization. This is because the equilibrium constant K_{eq} of aragonite ($10^{-8.34}$ at 25 °C and 1 atm.) is only slightly higher than K_{eq} of calcite ($10^{-8.48}$) which means that if one maintains a highly supersaturated solution w.r.t. calcite, to increase its precipitation rate, the solution would also be unavoidably supersaturated w.r.t. aragonite, which prevents aragonite dissolution. Similarity, if one maintains a highly undersaturated solution w.r.t. aragonite, to increase the dissolution rate, the solution would also be undersaturated w.r.t. calcite. One can, of course, start with a high degree of disequilibrium and let the solution drift freely towards equilibrium, yet in such a case the solution would quickly be buffered by aragonite dissolution and starts to oscillate around equilibrium. Therefore, aragonite to calcite stabilization must be studied near equilibrium, which leads to slow reaction rates. One solution to increase stabilization kinetics, which we adopted, is by increasing temperature because kinetics is directly proportional to temperature (Morse et al., 2007).

Increasing the reaction temperature in laboratory experiments comes at the expense of deviating from the natural conditions at which stabilization is postulated to occur. Temperature is known to exert significant impacts on reaction rates and Mg incorporation into calcite (e.g., Katz, 1973; Mucci, 1987). Regarding reaction rates, we do not think that our high temperature experiments, like nearly all other experiments, quantitatively resemble reaction rates in natural settings. However, that does not make our results inapplicable to understanding the natural diagenetic processes. Regarding Mg incorporation into calcite, the direct relationship between Mg incorporation into calcite and temperature is well documented (Mucci, 1987), suggesting that at lower temperatures, calcite would incorporate even less Mg but will certainly take longer time to form. Furthermore, our experiments used dilute solutions compared to pore-fluids in marine diagenetic environments which are derived from seawater. In seawater-like solutions, ion pairing, complexation, and the presence of organics and other chemical inhibitors can strongly impact calcite precipitation rate and Mg incorporation into calcite (Morse et al., 2007). Accordingly, caution must be taken when extrapolating our experimental results to natural systems.

5. Conclusions

This study uses laboratory experiments to demonstrate the effects of fluid:solid ratio (F:S) on aragonite to calcite stabilization (aragonite dissolution and calcite precipitation) in Mg-bearing fluids. The data show that lower F:S ratios: (i) enable stabilization of aragonite to calcite in Mg-bearing fluids, (ii) permit stabilization in fluids with higher [Mg] than has been previously shown possible, and (iii) lower the amount of Mg incorporated into calcite products. Taken together, these findings point to F:S as an important factor in controlling stabilization of carbonate sediments, with broad implications for where and how diagenetic calcites form in natural settings. First, the observations that stabilization (i.e., calcite growth) is inhibited by high [Mg] and F:S imply that stabilization does not occur in marine diagenetic environments that are hydrologically open to seawater. This leaves aragonite dissolution as the dominant process in these environments, which may represent an underrated source of alkalinity to the ocean. Second, stabilization from aragonite-rich sediments to calcite-rich limestones may be promoted by a decrease in the F:S and the development of a closed system. Such conditions occur naturally as burial increases, which leads to lower porosity and thus lower F:S as well as hydrologic isolation from seawater. The hypothesis that aragonite dissolution is the dominant process in open system diagenetic environments whereas aragonite stabilization to calcite dominates in closed system environments is supported by observations from natural settings and have important implications for studies that model the effect of diagenesis on geochemical proxies.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2021.117166.

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