Experimental constraints on nonskeletal CaCO$_3$ precipitation from Proterozoic seawater

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ABSTRACT

Precambrian carbonates record secular variations in the style of CaCO$_3$ nucleation and growth, yet the geochemical conditions recorded by some enigmatic textures remain poorly quantified. Here, we performed CaCO$_3$ nucleation experiments in synthetic seawater in order to constrain the mineralization pathways of synsedimentary calcite microspar cement, a prolific component of Proterozoic carbonates. We found that dissolved PO$_4$ above ~12 μmol/L (μM) inhibits the nucleation of aragonite and calcite and permits the formation of an amorphous Ca-Mg carbonate (ACMC) precursor once CaCO$_3$ supersaturation (Ω$_{CaCO_3}$) ≥ 45. Depending on seawater Mg/Ca, AMC is then rapidly recrystallizes to monohydrocalcite and/or calcite. This precipitation mechanism is consistent with sedimentological, petrographic, and geochemical characteristics of Proterozoic synsedimentary calcite microspar cement, and it suggests that kinetic interactions among common seawater ions may open nontraditional CaCO$_3$ mineralization pathways and sustain high CaCO$_3$ supersaturation.

INTRODUCTION

Before the advent of skeletal biomineralization, CaCO$_3$ production is thought to have been strongly influenced by inorganic processes. For example, distinctive sedimentary and early diagenetic fabrics documented in Precambrian rocks record secular variations in marine carbonate chemistry (Grotzinger and James, 2000); however, the specific chemical controls on abiotic CaCO$_3$ production are poorly constrained. A particularly enigmatic product in this regard is synsedimentary calcite microspar cement, a widespread and abundant primary pore-filling component of Mesoproterozoic to Neoproterozoic (Tonian) carbonates (Fig. 1; James et al., 1998). This cement comprises mosaics of equant 5–15 μm calcite crystals that share identical cathodoluminescence characteristics and preserve evidence for initial spheroidal particle precipitation with polygonal overgrowths (Fairchild and Spiro, 1987; Pollock et al., 2006). Sedimentological evidence indicates that these cements crystallized rapidly relative to surrounding sediment (e.g., James et al., 1998), while geochemical data and mass balance constraints indicate an origin from fluids dominated by contemporaneous seawater (Frank and Lyons, 1998; Bishop and Sumner, 2006). Unlike other late Proterozoic carbonate components that clearly preserve evidence of former aragonite (consistent with relatively high Mg/Ca in Tonian seawater; Spear et al., 2014), the primary mineralogy of microspar is unconstrained. The formation of calcite microspar cement has recently been suggested to have required CaCO$_3$ supersaturation (Ω$_{CaCO_3}$) greatly exceeding that of the modern ocean (Strauss and Tosca, 2020). The maintenance of CaCO$_3$ supersaturation through much of the Precambrian, by definition, would have required the inhibition and/or modification of CaCO$_3$ precipitation (i.e., Sumner and Grotzinger, 1996). This, in turn, suggests that before skeletons evolved, the rates and pathways of CaCO$_3$ production may have had a strong kinetic control. Although several compounds are known to inhibit or modify the precipitation of CaCO$_3$ (including Fe$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, SO$_4^{2-}$, PO$_4^{3-}$, and organic acids; Burton and Walter, 1990; Sumner and Grotzinger, 1996), relatively few studies have elucidated the sedimentologic consequences of kinetic inhibition. For example, PO$_4$ dramatically influences nucleation and growth kinetics at μM concentrations (i.e., Burton and Walter, 1990), and although observational data and theoretical models indicate both spatial and temporal variations in Precambrian PO$_4$ cycling (e.g., Laakso et al., 2020), the consequences for nonskeletal CaCO$_3$ production are virtually unknown. Here, we examined the influence of common seawater ions on the dynamics of CaCO$_3$ precipitation from Precambrian seawater, with a specific focus on dissolved PO$_4$.

METHODS

We examined CaCO$_3$ nucleation in the presence of PO$_4$ with two types of experiments conducted in synthetic Tonian seawater at 22 ± 1.5 °C and stirred at 250 rpm: (1) degassing experiments, and (2) constant composition experiments (Fig. S1 in the Supplemental Material). Synthetic Tonian seawater (based on fluid inclusion constraints; Spear et al., 2014) was prepared from reagent-grade salts, stock solutions, and deionized water (see Table S1). Total dissolved PO$_4$ (hereafter [PO$_4$]) ranged from 0 to 100 μM, the higher values of which exceed most modern carbonate sediment pore waters (which can reach >30 μM; Morse, 1985). In degassing experiments, nucleation thresholds were approached by saturating the solution with 10% CO$_2$ gas and fixing total alkalinity (TA). CO$_2$ was then degassed by N$_2$ purging, which increased Ω$_{CaCO_3}$ until nucleation occurred. Continuous monitoring of pH, with known [Ca$^{2+}$] and TA, constrained the carbonate chemistry at the point of nucleation. In constant composition experiments, the desired Ω$_{CaCO_3}$ dissolved inorganic carbon (DIC), ionic strength, and TA were kept constant via autotitration of CaCl$_2$ and Na$_2$CO$_3$ - NaHCO$_3$-NaOH titrants until CaCO$_3$ nucleation.

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RESULTS

Degassing and constant composition experiments showed that the \( \Omega_{\text{cal}} \) threshold at which CaCO\(_3\) nucleation occurs is strongly influenced by dissolved PO\(_4\) (Fig. 2; Tables S1C and S1D). Below 6 \( \mu M \) PO\(_4\), spontaneous CaCO\(_3\) nucleation occurred at \( \Omega_{\text{cal}} \) between 20 and 30 (Fig. 2); under the conditions examined here, this range was largely independent of DIC and TA. In contrast, at [PO\(_4\)] greater than \( \sim 12 \mu M \), CaCO\(_3\) nucleation was strongly inhibited, and the minimum threshold for CaCO\(_3\) nucleation corresponded to \( \Omega_{\text{cal}} \) of \( \sim 45 \) (Figs. 2 and 3). No detectable CaCO\(_3\) nucleation occurred below this threshold, even over extended experiment durations (19 d). For experiments where precipitation was observed, CaCO\(_3\) nucleation induction time (or the time elapsed between the establishment of supersaturation and nucleation) increased strongly with increased [PO\(_4\)] from 25 to 100 \( \mu M \) (Fig. 3).

The experiments also showed that dissolved PO\(_4\) strongly controlled the resulting CaCO\(_3\) polymorph precipitated from seawater solutions (Fig. 2). Specifically, below 6 \( \mu M \) [PO\(_4\)], aragonite was consistently produced. Above 6 \( \mu M \) PO\(_4\), no aragonite was observed, and precipitates were dominated by monohydrocalcite and/or Mg-calcite. Our data show that in the presence of PO\(_4\), monohydrocalcite is produced across a broad range of Mg/Ca and CO\(_3\)/Ca ratios; however, lower Mg/Ca and CO\(_3\)/Ca ratios promote Mg-calcite formation over monohydrocalcite (Fig. 2). XRD, \textit{in situ} Raman spectroscopy, and ex-\textit{situ} FT-IR analyses showed that in the presence of PO\(_4\), amorphous Ca-Mg-carbonate (ACMC) initially nucleated from solution and recrystallized to either monohydrocalcite and/or Mg-calcite (Figs. S2–S3) in minutes to hours (Fig. 4). Amorphous calcium phosphate (ACP) nucleated in experiments where PO\(_4\) approached 100 \( \mu M \) (along with ACMC), which recrystallized to octacalcium phosphate over 48 h (Fig. S3).

DISCUSSION

Our results indicate that [PO\(_4\)] above \( \sim 12 \mu M \) suppresses the spontaneous nucleation of aragonite and/or calcite in synthetic Tonian seawater, most likely through adsorption onto nascent particle nuclei and subsequent inactivation of growth sites (Burton and Walter, 1990). This permits the formation of ACMC under suitably saturated conditions, which explains several experimental observations. First, the
Figure 2. Results of CaCO$_3$ nucleation experiments in synthetic late Proterozoic seawater at 22 ± 1.5 °C with different Mg/Ca ratios. (A) Mg/Ca = 2.67, (B) Mg/Ca = 3.3, and (C) Mg/Ca = 5.56. Dashed gray contours represent CaCO$_3$ supersaturation ($\Omega_{\text{cal}}$) determined using apparent solubility product ($K_{\text{sp}}^*$) of calcite (10$^{-6.37}$ at 25 °C) in seawater based on concentrations (Mucci, 1983). Colored contours represent solubility product estimates of amorphous Ca-Mg carbonate (ACMC), where \( \log K_{\text{spACMC}} = 0.018 \times (\text{mol% Mg})^{-6.28} \) at 25 °C, at 30, 40, and 50 mol% Mg$^{2+}$ (Purgstaller et al., 2019). DIC—dissolved inorganic carbon; TA—total alkalinity. Data points represent crystalline polymorphs precipitated at corresponding solution compositions.

Figure 3. (A) Relationship between natural logarithm of measured CaCO$_3$ nucleation induction time ($t_{\text{ind}}$) and calculated saturation ratio, $S = \Omega_{\text{cal}}^{1/2}$, where $N$ = number of ions in AMC = 3(Ca$^{2+}$, Mg$^{2+}$, and CO$_3^{2-}$). (B) Relationship between calculated induction time and $\Omega_{\text{cal}}$. Gray shaded area indicates minimum nucleation threshold of $\Omega_{\text{cal}} = 45$ in seawater with elevated [PO$_4^{3-}$].
minimum $\Omega_{\text{calc}}$ nucleation thresholds observed in our experiments correspond closely with ACMC solubility estimates (Fig. 2; Purgstaller et al., 2019). ACMC solubility is a function of its Mg content, which is influenced by solution Mg/Ca, [PO$_4^3-$], and pH (Blue and Dove, 2015). Vibrational spectroscopy (Raman $v_1$ values) indicates that the ACMC formed in our experiments varied between 30 and 50 mol% Mg (i.e., Purgstaller et al., 2019; see Fig. 4).

The initial nucleation of ACMC in Tonian seawater (when [PO$_4$]$_{\text{tot}}$ > 12 $\mu$M) also reconciles experimental observations of CaCO$_3$ polymorph selection. ACMC is metastable and rapidly transforms to Mg-bearing calcite or monohydrocalcite (Blue et al., 2017). The resulting crystalline phase is dependent on the Mg content of ACMC, solution Mg/Ca, CaO/Ca, pH, and stirring rate (Blue et al., 2017; Purgstaller et al., 2019). Consistent with this, our observations indicate that lower Mg/Ca ratios promote calcite (Fig. 2), whereas higher Mg/Ca ratios promote monohydrocalcite. Although monohydrocalcite may also recrystallize to Mg-calcite (Fukushi and Matsumiya, 2018; Purgstaller et al., 2019), this pathway was not observed under the conditions examined here.

ACMC nucleation provides a simple explanation for an apparent CaCO$_3$ nucleation threshold in seawater when [PO$_4$]$_{\text{tot}}$ > 12 $\mu$M. Spontaneous CaCO$_3$ nucleation induction time has been shown to continuously increase with decreasing $\Omega_{\text{calc}}$ in modern seawater, as predicted by classical nucleation theory (CNT; Pokrovsky, 1998). Conversely, our experiments show that in seawater with elevated [PO$_4$]$_{\text{tot}}$, no nucleation occurs below a lower $\Omega_{\text{calc}}$ threshold of 45 (Fig. 3), even over time scales where nucleation should have occurred according to CNT. This result is consistent with molecular dynamic calculations of supersaturated CaCO$_3$ solutions (Wallace et al., 2013), which show that once a key $\Omega_{\text{calc}}$ threshold is crossed, amorphous CaCO$_3$ can form through the rapid production of dense liquid droplets. This liquid-liquid separation process occurs in a compositional regime that may only be accessed if the precipitation of crystalline polymorphs is suppressed.

ACMC-mediated precipitation pathways may, in turn, strongly influence the loci of CaCO$_3$ nucleation in marine systems where elevated PO$_4$ is present. In the modern ocean, inorganic CaCO$_3$ nucleation is often linked to the presence of microbial substrates (Robbins and Blackwelder, 1992). This is because nucleating calcite on a microbial substrate requires less energy than the direct nucleation of calcite from aqueous solution (e.g., Obst et al., 2009). However, in the presence of PO$_4$ (or other compounds that inhibit crystalline CaCO$_3$ nucleation), the energy barrier to ACMC nucleation is lower than the barrier to CaCO$_3$ nucleation on a foreign substrate (Wallace et al., 2013; De Yoreo et al., 2015). This in turn implies that foreign surfaces are unlikely to influence CaCO$_3$ nucleation thresholds in supersaturated systems where calcite and aragonite nucleation is inhibited, consistent with experimental and natural systems (Reddy and Hoch, 2012; Fukushi and Matsumiya, 2018), thus ACMC would be expected to nucleate where variations in temperature, pressure, and/or fluid composition exceed its solubility in natural systems.

Our experimental observations provide new insight into Precambrian nonskeletal carbonate sedimentation. Specifically, these experimental data begin to constrain the origin of fabrics associated with rapid CaCO$_3$ nucleation, such as synsedimentary calcite microspar cement (James et al., 1998). We hypothesize that the lack of petrographic evidence for former aragonite in late Proterozoic microspar (Fairchild and Spiro, 1987) is most consistent with ACMC nucleation and subsequent transformation to calcite (Bishop and Sumner, 2006). Spheroidal cores and crystal size distributions observed in microspar cement are also consistent with Ostwald ripening of an ACMC precursor formed at high $\Omega_{\text{calc}}$ values (greater than 69–100; Kile and Eberl, 2003), as is enhanced Sr incorporation into the resulting calcite because ACMC favors trace-element uptake (Littlewood et al., 2017). Together, these observations support the hypothesis that microspar cement reflects precipitation pathways enabled only under high $\Omega_{\text{calc}}$ (Strauss and Tosca, 2020).

Crucially, it is the suppression of aragonite and calcite in marine systems that enables ACMC formation, which in turn opens subsequent recrystallization pathways to CaCO$_3$. Although Fe$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, SO$_4^{2-}$, or organic acids may modify CaCO$_3$ growth rates, they are not known to suppress aragonite nucleation at high Mg/Ca (Bots et al., 2011). Thus, among known inhibitors, PO$_4$ is likely to have influenced shallow-water CaCO$_3$ production through much of the Proterozoic. In fact, elevated [PO$_4$]$_{\text{tot}}$ has been shown to maintain high $\Omega_{\text{calc}}$ and lead to the production of metastable precursors in several synthetic and natural systems (Gallagher et al., 2013; Lin et al., 2018), including many alkaline lakes (Bischoff et al., 1993; Fukushi and Matsumiya, 2018). These observations, in combination with our experimental data, suggest that the stratigraphic distribution of depositional fabrics reflecting high $\Omega_{\text{calc}}$, such as microspar, and possibly cap carbonates and giant ooids (Grotzinger and James, 2000; Trower, 2020), could together reflect kinetic controls on CaCO$_3$ precipitation through the effects of elevated pore and/or bottom water [PO$_4$]. Although shale-hosted geochemical records indicate relatively minor perturbations to net P flux through much of the Precambrian (including intervals of global phosphogenesis; Laakso et al., 2020), pore/bottom water [PO$_4$] may have been most strongly influenced by the degree of internal PO$_4$ recycling (Ingall et al., 1993) and/or the apatite burial efficiency controlled by seawater [Ca$^{2+}$] (e.g., Zhao et al., 2020). Although the details of PO$_4$ cycling and burial in Precambrian CaCO$_3$ depositional environments are poorly constrained, Tonian Carbonate biominalerizing organisms (Cohen et al., 2017) record enhanced P availability in the water column at a time when synsedimentary microspar peaked in its stratigraphic distribution (James et al., 1998).

CONCLUSIONS

Our data show that kinetic interactions among common seawater ions may generate nontraditional mineralization pathways that
offer new explanations for enigmatic Precambrian carbonate fabrics such as synsedimentary calcite microspar cement; thus, future interpretations of isotopic and trace-elemental variations in Precambrian carbonates should take explicit account of these CaCO₃ mineralization pathways and their associated expressions. More broadly, our data show that because [PO₄] strongly increases nucleation thresholds, while effectively arresting the growth rates of preexisting CaCO₃ (Mucci, 1986), periods of enhanced PO₄ recycling, whether driven by ecological factors (Lenton and Daines, 2018) or ocean-atmosphere redox (Laakso et al., 2020), may significantly alter the dynamics of atmosphere redox (Lenton and Daines, 2018), may effectively arresting the growth rates of preexist CaCO₃ (Mucci, 1986), periods of enhanced PO₄ recycling, whether driven by ecological factors (Lenton and Daines, 2018) or ocean-atmosphere redox (Laakso et al., 2020), may fundamentally altered the dynamics of Precambrian Eon.

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