Mineralogical constraints on Neoproterozoic $p\text{CO}_2$ and marine carbonate chemistry

Justin V. Strauss¹ and Nicholas J. Tosca²

¹*Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, USA*

²*Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN, UK*

ABSTRACT

Numerous investigators have sought to identify what perturbations to the global carbon cycle fueled Earth system change during the Neoproterozoic Era. Nevertheless, a lack of constraints on ocean-atmosphere carbon chemistry has precluded efforts to link biology, climate, and the lithosphere. We combine field and petrographic observations with experimental and theoretical geochemistry to show that early Neoproterozoic seawater featured elevated alkalinity in the presence of high atmospheric $p\text{CO}_2$, which sustained remarkable marine CaCO_3 supersaturation (Ω_{Calcite}). Without pelagic calcification, Neoproterozoic marine Ω_{Calcite} and $p\text{CO}_2$ would have been mediated principally by CaCO_3 precipitation kinetics; thus, secular changes in kinetic inhibitors to CaCO_3 nucleation may have destabilized the global carbon cycle.

INTRODUCTION

The Neoproterozoic Era represents a dynamic interval in the long-term evolution of Earth's carbon cycle, largely reflected by volatility in the carbon isotopic composition of carbonate rocks. These isotopic perturbations are commonly thought to reflect episodic burial and oxidation of a reduced carbon pool, although this simplified model has been challenged by modeling and geochemical datasets (e.g., Bristow and Kennedy, 2008). Nevertheless, all models

for the Neoproterozoic carbon cycle suffer from an absence of quantitative constraints on ocean-atmosphere carbon chemistry, which prohibits an understanding of how CaCO_3 burial may have regulated Earth's surface carbon reservoir.

Geologists have long recognized that the varying styles of nucleation and crystal growth preserved in Precambrian carbonate rocks reflect secular changes in CaCO_3 production (Grotzinger and James, 2000). For example, Mesoproterozoic and early Neoproterozoic carbonates record the progressive replacement of Archean and early Proterozoic seafloor precipitates by sediment derived almost exclusively from microcrystalline CaCO_3 (Grotzinger and James, 2000). Yet, the conditions that shifted marine CaCO_3 production to water column nucleation, and how this impacted the global carbon cycle, are unknown. Here, we combine field and petrographic data with experimental and theoretical geochemistry to derive solutions for marine carbonate chemistry during two intervals of the Tonian (~1,000–720 Ma).

BACKGROUND AND METHODS

Like other Tonian successions, the ~805–788 Ma Svanbergfjellet (Svalbard, Norway) and ~755–735 Ma Callison Lake (Yukon, Canada) formations (fms; Fig. 1) are constructed mainly from carbonate mud, lithoclasts, and stromatolites (Knoll and Swett, 1990; Strauss et al., 2015); however, they differ slightly from other successions in that they also contain discrete intervals of abundant Mg-silicates (Tosca et al., 2011). The Svanbergfjellet Formation (Fm) was deposited in open marine subtidal to peritidal settings (Knoll and Swett, 1991) and hosts abundant molar tooth structures and laminae that are filled with penecontemporaneous Mg-silicate and CaCO_3 microspar (Fig. 2; Tosca et al., 2011). Molar tooth structures are enigmatic early diagenetic mm- to dm-long veins and contorted lenses of CaCO_3 microspar that are unique to the Precambrian sedimentary record (e.g., James et al., 1998). In contrast, talc-bearing strata of the Callison Lake

Fm were deposited in episodically restricted marine environments and notably lack molar tooth structures and/or CaCO_3 microspar (Strauss et al., 2015). Although Tosca et al. (2011) interpreted Callison Lake Mg-silicates as diagenetic, Strauss et al. (2015) described talc-rich mudstone and microbial dolostone facies with Mg-silicate ooids, oncolites, and intricately draped stromatolites (Fig. 2C) that support contemporaneous Mg-silicate and CaCO_3 precipitation. Both successions host paleontological and chemostratigraphic data that support marine settings, indicating that Mg-silicate authigenesis characterized both open and restricted Tonian basins (GSA Data Repository¹).

We analyzed samples from the Callison Lake and Svanbergfjellet fms via optical petrography and powder X-ray diffraction (XRD). XRD was performed at the University of Oxford on a Panalytical Emperean Series 2 instrument. We also performed equilibrium carbonate chemistry calculations and reaction path models of evaporation with MATLAB and Geochemist's Workbench v11.0 using thermodynamic data from Zeebe and Wolf-Gladrow (2001), Harvie et al. (1984), and He & Morse (1993) (GSA Data Repository¹).

NEOPROTEROZOIC CARBONATE CHEMISTRY

The authigenic precipitation of Mg-silicates requires a distinct combination of physio-chemical conditions; experimental investigations have delineated a supersaturation threshold required to nucleate Mg-silicates directly from seawater-type solutions, which show that kinetically, pH is the principal control on Mg-silicate precipitation (Tosca et al., 2011). Regardless of $[\text{Mg}^{2+}]$ and $[\text{SiO}_2(aq)]$, spontaneous nucleation of Mg-silicates is kinetically inhibited below a pH of 8.5, an observation that is quantitatively supported by the strong exponential dependence of nucleation rates on supersaturation (Tosca et al., 2011). Thus, in order for the Svanbergfjellet and Callison Lake basins to have maintained pH at sufficient levels

to precipitate penecontemporaneous CaCO_3 and Mg-silicates, water chemistry must have been characterized by a total alkalinity pool that was greater than twice that of $[\text{Ca}^{2+}]$ ($[\text{ALK}] > 2*[\text{Ca}^{2+}]$; Al-Droubi et al., 1980; Lazar et al., 1983). This constraint arises because any CaCO_3 precipitated before or during Mg-silicate authigenesis will decrease total alkalinity by a factor of two relative to $[\text{Ca}^{2+}]$; thus, during episodes of basinal restriction in the Callison Lake Fm, residual alkalinity must have remained in solution after chemically induced CaCO_3 precipitation.

The equilibrium carbonate system can be solved if any two of six chemical variables are known (pH, $[\text{ALK}]$, $[\text{CO}_2(aq)]$, $[\text{CO}_3^{2-}]$, $[\text{HCO}_3^-]$, and DIC, assuming 25°C, 1 bar, and modern marine ionic strength). Regardless of how total alkalinity was modified during restriction of the Callison Lake basin, a minimum pH of 8.5, in combination with the $[\text{ALK}] > 2*[\text{Ca}^{2+}]$ constraint, defines a solution space for the carbonate system that is dependent on $[\text{Ca}^{2+}]$ at the onset of evaporation (Table 1). Because preservation of CaCO_3 sediment requires $\Omega_{\text{Calcite}} > 1$, the minimum permissible $[\text{Ca}^{2+}]$ in the restricted Callison Lake basin translates to 1.2 mmol/kg, and the maximum $[\text{Ca}^{2+}]$ must have been lower than open marine values because Mg-silicates do not occur in open marine carbonates of the Callison Lake Fm or other contemporaneous basins. Experimental geochemistry has shown that $\Omega_{\text{Calcite}} = 20$ is required to spontaneously produce CaCO_3 from marine-derived waters (Morse and He, 1993). This provides a generous upper limit for Ω_{Calcite} of the restricted basin, which equates to maximum $[\text{Ca}^{2+}]$ of 5 mmol/kg. This constraint is consistent with a conspicuous lack of depositional fabrics in the Callison Lake Fm that indicate unusually high supersaturation such as CaCO_3 microspar (James et al., 1998; Kile et al., 2000; Bishop and Sumner, 2006). Assuming that Callison Lake basinal waters maintained connection with the atmosphere during restriction (Lazar et al., 1983), the resulting range in $p\text{CO}_2$ (165-724 ppmv) allows us to constrain the carbonate chemistry of open marine systems

during Callison Lake sedimentation based on marine $[\text{Ca}^{2+}]$. Reaction path model simulations of seawater evaporation show that at even with modern $[\text{SO}_4^{2-}]$ (and modern $[\text{Na}^+]$ and $[\text{Cl}^-]$), gypsum/anhydrite will precipitate before halite as long as $[\text{Ca}^{2+}] > 6 \text{ mmol/kg}$ (Table 1; GSA Data Repository¹). At higher $[\text{Na}^+]$ and $[\text{Cl}^-]$ or lower $[\text{SO}_4^{2-}]$, this limit increases. Combining these constraints and assuming open marine Ω_{Calcite} was between 1-20 suggests marine DIC concentrations ranged from 0.697-7.29 mmol/kg and pH from 7.8-8.5 (Fig. 3).

Unlike the Callison Lake Fm, Mg-silicates of the Svanbergfjellet Fm occur in subtidal limestone facies of an open marine carbonate ramp (GSA Data Repository¹). Here, fine-grained nodular aggregates of Mg-silicates are intimately associated with microcrystalline CaCO_3 composed entirely of euhedral 10-15 μm interlocking crystals (Fig. 2D-F), a fabric petrographically identical to “microspar cement” (James et al., 1998; Grotzinger and James, 2000; Bishop and Sumner, 2006); however, instead of being solely confined to molar-tooth void space, Svanbergfjellet CaCO_3 microspar also forms laterally continuous laminae and beds (Fig. 2D). Petrographic examination indicates the CaCO_3 microspar-Mg-silicate assemblage precipitated contemporaneously through physical separation instead of diagenetic replacement or displacive growth, most likely due to surface charge disparities resulting from the hydrophobic nature of Mg-silicates (Fig. 2E-F; GSA Data Repository¹). These distinctive textures, in combination with the presence of Mg-silicate coated grains and stromatolites and reworked CaCO_3 microspar-Mg-silicate aggregates, require Mg-silicate precipitation from the water column or at the sediment-water interface, not within the sediment during early diagenesis. This inference is also supported by Ca mass balance: significant volumes of seawater are required to precipitate enough CaCO_3 prior to compaction (Bishop and Sumner, 2006).

Fluid inclusion data from the >830 Ma Browne Fm of Australia (Hill et al., 2000) constrains Tonian seawater $[Ca^{2+}]$ to 9-12 mmol/kg, and age-equivalent gypsum-before-halite evaporites establish a minimum value of 6 mmol/kg (Spear et al., 2014). Using these constraints and the same geochemical reasoning for Mg-silicate precipitation outlined above (Table 1), this implies that during Svanbergfjellet sedimentation, marine DIC was 10-20 mmol/kg, atmospheric pCO_2 ranged from 870-1760 ppmv, and Ω_{Calcite} at the time of $CaCO_3$ microspar nucleation ranged from 30-116 (Fig. 3). Because the >830 Ma Browne Formation fluid inclusions are $[Ca^{2+}]$ -enriched but depleted in alkalinity and SO_4 , their parent waters must have had $[ALK] < 2*[Ca^{2+}]$ (Spear et al., 2014); these constraints indicate that the total alkalinity of Tonian seawater surpassed the $[ALK] > 2*[Ca^{2+}]$ threshold between >830 and 805 Ma.

DISCUSSION

Together, these data indicate that Precambrian ocean-atmosphere chemistry and the controls on $CaCO_3$ production were potentially much different than commonly assumed. First, seawater Ω_{Calcite} , at least periodically, exceeded that of the modern ocean or any known interval of the Phanerozoic (Morse et al., 2003; Zeebe and Westbroek, 2003; Higgins et al., 2009). Second, the Ω_{Calcite} values obtained for the spontaneous nucleation of $CaCO_3$ microspar are far higher than the nucleation threshold associated with abiotic $CaCO_3$ nucleation from modern seawater despite similar major element compositions (Morse and He, 1993). Finally, if our results are applicable to $CaCO_3$ microspar precipitation more generally, then the stratigraphic abundance of this unique sedimentary component indicates that seawater or early diagenetic pore waters repeatedly crossed this Ω_{Calcite} threshold throughout the Proterozoic (James et al., 1998).

Dominantly abiotic nucleation of $CaCO_3$ is rare in the modern ocean; when it occurs, spontaneous nucleation is often associated with cyanobacterial biomass (Robbins and

Blackwelder, 1992). This is because at the Ω_{Calcite} values typical of the surface ocean (~4-7), cyanobacterial surfaces reduce the surface free energy associated with direct CaCO_3 nucleation from seawater (Söhnel & Mullin, 1982; Obst et al., 2009); however, in the presence of compounds that inhibit or modify CaCO_3 precipitation, the threshold for nucleation, mineralization pathway, and effect of foreign surfaces may be altered. Reddy and Hoch (2012) documented a CaCO_3 nucleation threshold of $\Omega_{\text{Calcite}} > 100$ for a modern alkaline lake despite steady state Ω_{Calcite} values of 6-38 (Fukushi and Matsumiya, 2018). These authors observed that the presence of cyanobacterial material made no statistical difference in modifying the nucleation threshold, indicating that inhibiting compounds and/or high Ω_{Calcite} may permit lower energy pathways to CaCO_3 nucleation.

We hypothesize that the episodic to long-term ($>10^6$ yr) maintenance of high CaCO_3 supersaturation requires the presence of kinetic inhibitors in Neoproterozoic seawater that influenced CaCO_3 precipitation by: 1) retarding growth on pre-existing substrates (Meyer, 1984), and 2) increasing the critical supersaturation necessary for CaCO_3 nucleation (Söhnel and Mullin, 1982; Dromgoole and Walter, 1990). Although our analysis does not constrain the identity of inhibiting compounds, Fe^{2+} , Mn^{2+} , SO_4^{2-} , PO_4^{3-} , organic acids, alkalinity, and $p\text{CO}_2$ all strongly influence the kinetics of CaCO_3 precipitation (Dromgoole and Walter, 1990; Grotzinger and Kasting, 1993; Sumner and Grotzinger, 1996). The identification of alternative low energy/high- Ω_{Calcite} pathways to CaCO_3 nucleation may also explain some of the unusual sedimentary textures and geochemical signatures of the Neoproterozoic. For example, the crystal size distribution of Neoproterozoic CaCO_3 microspar records recrystallization of a CaCO_3 precursor (Kile and Eberl, 2003), which based on CaCO_3 nucleation experiments can only be produced at Ω_{Calcite} values greater than 69-100 (Kile et al., 2000; Kile and Eberl, 2003). These

supersaturation levels exceed the solubility of amorphous CaCO_3 (ACC; Purgstaller et al., 2019), a commonly observed precursor associated with low surface free energy that is known to rapidly recrystallize to calcite through Ostwald ripening (e.g., Bots et al., 2012; Carino et al., 2017); thus, CaCO_3 microspar may not only indicate episodes of remarkable seawater Ω_{Calcite} , but also provide direct evidence of alternative pathways to abiotic CaCO_3 nucleation.

Because pelagic calcification was absent from Neoproterozoic oceans, alkalinity, DIC, and $p\text{CO}_2$ would have been strongly linked to the precipitation kinetics of CaCO_3 in shallow marine settings, and thus susceptible to perturbations in the magnitude of this sink (Ridgwell et al., 2003). As a result, the functional dependence of the CaCO_3 removal flux on Ω_{Calcite} may have strongly controlled the Neoproterozoic DIC pool and the relative partitioning of carbon burial between organic and inorganic forms. For example, if the production of new CaCO_3 was controlled by nucleation, and thus highly non-linear, then steady state marine carbonate chemistry may have been poised above a critical Ω_{Calcite} for $\sim 10^4$ -yr timescales (Zeebe and Westbroek, 2003), potentially perturbing the long-term carbon cycle (Ridgwell et al., 2003). In addition, global CaCO_3 precipitation fluxes in shallow-water carbonate systems, whether influenced by sea-level changes (Ridgwell et al., 2003) or fluctuations in the delivery of inhibiting compounds, were inextricably linked to global atmospheric $p\text{CO}_2$ and climatic stability. Finally, periods of excessive CaCO_3 supersaturation may have imposed environmental pressure on eukaryotes to develop mechanisms to control unwanted calcification, establishing a potential biochemical impetus for eukaryotic biomineralization. This is consistent with the observation that anti-calcifying molecules were already present in the last common ancestor to cnidarians and bilaterian animals and later recruited by biomineralizing organisms of the Ediacaran–Cambrian (Marin et al., 1996).

CONCLUSIONS

The contemporaneous precipitation of authigenic Mg-silicates and CaCO_3 is most simply viewed as a key threshold in marine (or non-marine) alkalinity, likely triggered by secular changes in CaCO_3 precipitation kinetics, and consistent with the sedimentary record of Precambrian carbonate rocks. Available data indicate that this threshold was reached multiple times throughout the Neoproterozoic, but apparently at no other time before or after; thus, unraveling carbonate chemistry through this interval has exposed the mechanistic underpinning of a dynamic inorganic carbon cycle unknown from any other period in Earth's history.

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FIGURE CAPTIONS

Figure 1. **A)** Neoproterozoic stratigraphy of the Ogilvie Mountains, Yukon, Canada, after Strauss et al. (2015). **B)** Proterozoic geology of Yukon and Northwest Territories (NWT). **C)** Pre-Devonian basement provinces in Svalbard, Norway, after Halverson et al. (2018). **D)** Neoproterozoic stratigraphy of northeastern Svalbard. Gp—Group; SG—Supergroup; Fm.—Formation; Mb.—Member; u.—Upper; l.—Lower.

Figure 2. X-ray diffraction (XRD) profiles and images of Mg-silicate-bearing carbonate strata in the Callison Lake and Svanbergfjellet fms. **A)** XRD profile of randomly oriented talc-rich samples. Blue dots indicate talc peaks; C: Calcite; D: Dolomite; Q: Quartz. **B)** Mg-silicate-bearing strata of the Callison Lake Fm with tents arrowed. **C)** Talc-coated oncolite in the Callison Lake Fm displaying alternating layers of Mg-silicate/organic matter (dark) with carbonate (light). Cross-cutting veins and fractures filled with silica cement. **D)** CaCO₃ microspar, dolosiltite, and molar tooth structure with nodular aggregates of Mg-silicates and CaCO₃ intraclasts from the Svanbergfjellet Fm; coin is 21 mm in diameter. **E)** Microcrystalline CaCO₃ and nodular talc aggregates in the Svanbergfjellet Fm with **F)** showing aggregation and physical separation of Mg-silicate crystallites from the surrounding CaCO₃ matrix.

Figure 3. Modelling solutions for Tonian and modern seawater carbonate chemistry with **A)** DIC vs. pH, and **B)** pCO₂ vs. pH. Seawater constraints for the Callison Lake and Svanbergfjellet fms derived from Table 1 and GSA Data Repository¹ with [Ca²⁺] reflecting marine conditions.

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346 www.geosociety.org/pubs/ft20XX.htm, or on request from editing@geosociety.org or
347 Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

Figure 1

Figure 3

Table 1. Marine Carbonate System Input Parameters

Unit	Age (Ma)	pH ^a	[Ca ²⁺]	Alkalinity ^c	<i>p</i> CO ₂	Omega (CaCO ₃)
Callison Lake Formation	~755–735					
<i>Open Marine</i>		<8.5	> 6 mmol ^b	>2*[Ca ²⁺]	<i>165–724 ppmv</i>	1–20
<i>Restricted Basin</i>		>8.5	1.2–5 mmol ^c	>2*[Ca ²⁺]	<i>165–724 ppmv</i>	1–20
Svanbergfjellet Formation	~805–788	>8.5	6–12 mmol ^d	>2*[Ca ²⁺]	<i>872–1750 ppmv</i>	<i>29–115</i>

^aKinetic constraints on Mg-silicate nucleation; ^bTime-equivalent gypsum-before-evaporite deposits;

^c[Ca²⁺] required to yield Ω_{calcite} from 1–20; ^dFluid inclusion data combined with constraint from ^b;

^eContemporaneous CaCO₃ and Mg-silicate precipitation; Imposed values in regular font and calculated values in italics.