

**Experimental examination of the Mg-silicate-carbonate system at ambient temperature:  
Implications for alkaline chemical sedimentation and lacustrine carbonate formation**

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**Abstract**

Despite their clear economic significance, Cretaceous presalt carbonates of the South Atlantic continental margins are not well-described by published facies models. This knowledge gap arises, in part, because the chemical processes that generate distinctive sedimentary products in alkaline, non-marine environments are poorly understood. Here, we use constraints inferred from reported mineralogical and geochemical features of presalt carbonate rocks to design and perform a suite of laboratory experiments to quantify the processes of alkaline chemical sedimentation. Using real-time observations of in-situ fluid chemistry, post-experiment analysis of precipitated solids, and geochemical modeling tools, we illustrate that spherulitic carbonates and Mg-silicate clays observed in presalt carbonates were likely precipitated from elevated pH (~10-10.5) waters with high concentrations of silica and alkali cations typical of intermediate to felsic rocks, such as Na<sup>+</sup> and K<sup>+</sup>. Charge balance constraints require that these cations were not counterbalanced to any significant degree by anions typical of seawater, such as Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, which implies minimal seawater involvement in presalt deposition. Experimental data suggest that, at this alkaline pH, only modest concentrations (i.e., ~0.5-1 mmol/kg) of Ca<sup>++</sup> would have been required to precipitate spheroidal CaCO<sub>3</sub>. Given the rapid rates of CaCO<sub>3</sub> nucleation and growth under such conditions, it is unlikely that Ca<sup>++</sup> concentrations in lake waters ever exceeded these values, and sustained chemical fluxes are therefore required for extensive

sediment accumulation. Moreover, our experiments indicate that the original mineralogy of presalt  $\text{CaCO}_3$  could have been calcite or aragonite, but the differing time scales of precipitation between  $\text{CaCO}_3$  and Mg-silicates would have tended to skew the Mg/Ca ratio in solution towards elevated values which favor aragonite. Mg-silicate nucleation and growth rates measured during our experiments suggest that elevated  $\text{SiO}_2(\text{aq})$  and high pH would have limited (to 1-2 mmol/kg) the  $\text{Mg}^{++}$  concentrations required to precipitate poorly crystalline Mg-silicates, which, through time, crystallize to minerals such as sepiolite and stevensite. Although our results provide robust constraints on the geochemistry of Mg-silicate-carbonate interactions during alkaline lake sedimentation, they leave open the potential for biological contributions to sedimentation within the presalt basins, as well as the hydrogeochemical mechanisms that maintained a productive carbonate factory of the scale observed along the South Atlantic margins.

## **1. Introduction and motivation**

Relatively thick carbonate successions of Cretaceous age, deposited on the South American and African margins, host some of the most significant petroleum reservoirs discovered in decades. These rocks are thought to have formed in a variably restricted or non-marine depositional setting (e.g., Chitale et al., 2015; Wright and Barnett, 2015; Saller et al., 2016), and host carbonate and authigenic silicate minerals displaying a variety of unusual fabrics and sedimentary textures. Because of their economic importance, research has increasingly focused on tackling the challenging problem of describing the environments in which they formed (Bertani and Carozzi, 1985a; Bertani and Carozzi, 1985b; Carminatti et al., 2008; Wright, 2012; Chitale et al., 2015; Thompson et al., 2015; Tosca and Wright, 2015; Saller et al., 2016). Nonetheless, the unique authigenic mineralogical assemblages of these reservoirs have

comparatively few analogues within the geologic record, which has prevented the development of comprehensive facies descriptions that exist for many marine carbonates. A principal hurdle is that, although biological influences most likely played a role, the generation of non-marine carbonates is strongly influenced by depositional chemistry. Thus, a detailed understanding of the geochemical processes that influence mineral formation in these environments will underpin the development of new facies models that integrate both sedimentology and geochemistry.

## **1.1 The presalt carbonates**

Although the geochemistry of rift-related lakes—particularly those associated with the East African Rift—has been extensively studied for some time in the context of paleoclimatological records (e.g., Eugster and Hardie, 1978; Cerling, 1994), relatively little attention has been given to the development of facies models that can help to hone in on geochemical factors that affect the characteristics and productivity of hydrocarbon reservoirs. This intellectual gap prompted Wright (2012) to highlight the shortcomings of existing lacustrine carbonate facies models to accommodate either the diverse nature of microbial interactions in lacustrine carbonates or the effects of tectonic/volcanic processes on the coexisting lacustrine carbonate factory. Since then, advancements in the qualitative understanding of textural features of these reservoirs has greatly increased through detailed analysis of core samples, well log data, and outcrop samples from both ancient and modern analogues (Wright, 2012; Awramik and Buchheim, 2015; Chitale et al., 2015; Thompson et al., 2015; Tosca and Wright, 2015; Saller et al., 2016).

The non-marine carbonate sequences of interest formed prior to a major phase of evaporite deposition (herein termed “presalt”) within “syn-rift” and “sag” phase alkaline lakes associated with the rifting of Western Gondwana. Several of these basins were at least partially

filled by thick continental flood basalts (Thompson et al., 2015). Wright and Barnett (2015) outlined a depositional model for the presalt carbonates of the Santos Basin, offshore Brazil, which consists of cycles of three texturally distinct sub-facies: 1) spherulitic  $\text{CaCO}_3$  in a Mg-silicate rich matrix (“spherulites”, Fig. 1); 2) calcium carbonate shrubs (“shrubs”); and 3) mud-grade laminated carbonates (“laminites”). The spherulite facies contains calcite spherules generally under ~3 mm in diameter (published images suggest typical spherule diameters of around several hundred micrometers (Terra et al., 2010; Wright and Barnett, 2015; Saller et al., 2016)) embedded in a Mg-silicate matrix (Wright and Barnett, 2015); shrub successions contain upward-branching mm to cm-scale  $\text{CaCO}_3$  shrubs which appear to have nucleated on the paleo-lake bottom and grown upward; and laminite facies are generally under 0.3 m thick, commonly silicified, and composed of fine-grained detrital limestones with well-preserved fish fossils (Wright and Barnett, 2015) suggestive of a more circum-neutral pH during deposition (Alabaster and Lloyd, 2013).

Wright and Barnett (2015) interpreted these cyclic facies associations as reflecting evaporation and freshening events. They hypothesized that evaporative concentration triggered the formation of authigenic Mg-silicates and influenced the growth morphology of carbonate minerals, while freshening led to silica deposition and decreased Mg-silicate precipitation. At a basic level, however, in order for evaporative concentration of lake and/or marine water to generate observed mineral products as hypothesized, a number of geochemical conditions must be met (Eugster and Hardie, 1978; Eugster and Jones, 1979), which places strong constraints on the nature and evolution of the presalt depositional system. Unraveling these, in turn, requires an improved understanding of Mg-silicate-carbonate precipitation kinetics and growth behavior under a wide variety of conditions. Most importantly, although the geochemistry of Mg-silicate

precipitation has received some attention in recent years (e.g., Deocampo, 2005; Tosca et al., 2011; Bristow et al., 2012; Tosca and Masterson, 2014), the attendant effects on carbonate precipitation are poorly understood. To this end, a primary goal of this study is to place enhanced constraints upon the geochemical processes leading to coupled Mg-silicate and carbonate growth from alkaline depositional systems, with the aim of assisting in the development of facies models that will influence ongoing exploration efforts.

## **2. Mg-silicate-carbonate interactions during lake water evaporation**

In a particularly relevant study, Darragi and Tardy (1987) evaluated the evaporative concentration of Lake Yoa (part of the Lake Chad system) and concomitant precipitation of Mg-silicates,  $\text{CaCO}_3$ , and amorphous silica. In the shallow African lakes they studied, the water is in free contact with the atmosphere and the partial pressure of  $\text{CO}_2$  ( $p_{\text{CO}_2}$ ) is buffered at  $\sim 10^{-3.0-3.5}$  bar. As the waters become increasingly concentrated through evaporation, the  $p_{\text{CO}_2}$  remains approximately constant and the lake water pH increases. Concomitantly, thermodynamic thresholds are crossed such that  $\text{CaCO}_3$  begins to precipitate and control the solution  $\text{Ca}^{++}$  activity. Eventually, after critical pH and  $\text{Mg}^{++}$  and  $\text{SiO}_2$  concentration thresholds are crossed, Mg-silicates precipitate and set solution  $\text{Mg}^{++}$  activity, and amorphous silica precipitates and control solution  $\text{SiO}_2(\text{aq})$  activity. Roughly, the concentrations in the Lake Yoa solutions determined by Darragi and Tardy (1987) to mark the initiation of stevensite precipitation are  $\sim 1$  mmol/kg Mg, Ca, and  $\text{SiO}_2$ , with the concentrations of Mg and Ca gradually decreasing to values under 100  $\mu\text{mol/kg}$ , and the concentration of  $\text{SiO}_2$  increasing to values as high as 22 mmol/kg as evaporation proceeds. Throughout this stage of lake water evolution, the measured pH remains steady at  $\sim 10 \pm 0.3$ . Importantly, their analyses also show that concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{--}$  increase dramatically as the evaporative concentration process continues; however, the

concentrations of these important charged species are not eventually set by a mineral solubility constraint. Using a simple geochemical speciation model, Darragi and Tardy (1987) showed that evaporation and the precipitation of carbonate minerals and Mg-silicates, as well as the coupled evolution of lake water chemistry, can be modeled for the Lake Yoa system. Importantly, they show that while the concentration of Ca appears to be set by aragonite (the dominant  $\text{CaCO}_3$  mineral entering Lake Yoa sediments), Mg in solution appears to be controlled by the growth of stevensite.

## 2.1 Carbonate-alkalinity systematics during evaporation

The precipitation of both  $\text{CaCO}_3$  and Mg-silicate minerals during lake evaporation directly results from chemical interplays during evaporative concentration. The pH of evaporating waters is directly linked to its alkalinity, which is, in essence, a charge balance parameter defined for many natural waters according to (Stumm and Morgan, 1996):

$$\begin{aligned} [\text{Alkalinity}] &= [\text{HCO}_3^-] + 2 [\text{CO}_3^{--}] + [\text{OH}^-] - [\text{H}^+] \\ &= [\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{++}] + 2[\text{Mg}^{++}] - [\text{Cl}^-] - 2 [\text{SO}_4^{--}] - 2 [\text{NO}_3^{--}] \end{aligned} \quad (1)$$

The inorganic carbon system as represented by Eqn. 1 provides important first-order constraints on the chemical behavior of lakes during evaporative concentration. Because energetic barriers prevent the spontaneous precipitation of Mg-carbonates such as (hydro)magnesite (e.g., Giammar et al., 2005; Case et al., 2011; Berninger et al., 2014) and dolomite (e.g., Land, 1998) at low temperature and because other cations tend to behave conservatively,  $\text{Ca}^{++}$  is the only cation in natural waters removed from solution (as  $\text{CaCO}_3$ ) in the early stages of evaporation (Eugster and Hardie, 1978; Stumm and Morgan, 1996). For most Ca-bearing natural waters,  $\text{CaCO}_3$  grows as pH increases during the initial stages of evaporation. Then, as the solution

evaporates and  $\text{CaCO}_3$  continues to grow, the pH will behave in one of the following ways: 1) If  $2[\text{Ca}^{++}] > [\text{Alkalinity}]$  (e.g., modern seawater, where the net alkalinity balance includes significant concentrations of cations ( $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) and anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{--}$ ) *other than*  $\text{Ca}^{++}$  and  $\text{HCO}_3^-$ ), the pH will increase until the point of  $\text{CaCO}_3$  saturation, level off as  $\text{CaCO}_3$  growth keeps up with evaporative concentration, and finally decline as pH and alkalinity decreases and  $\text{Ca}^{++}$  increases; 2) If  $2[\text{Ca}^{++}] = [\text{Alkalinity}]$  (e.g., a  $\text{Ca}^{++}$ - $\text{HCO}_3^-$  water), then the pH will rise until the solution reaches  $\text{CaCO}_3$  saturation and then stabilize along with the concentrations of  $\text{Ca}^{++}$  and  $\text{CO}_3^{--}$ ; or 3) If  $2[\text{Ca}^{++}] < [\text{Alkalinity}]$  (i.e.,  $\text{Ca}^{++}$  is *not* the dominant alkalinity-producing cation), the pH will increase in close association with the increasing solution alkalinity (Eqn. 1). It follows that only the third scenario, in which  $[\text{Ca}^{++}] < 0.5[\text{Alkalinity}]$ , will lead to significantly elevated pH (i.e.,  $\text{pH} \gtrsim 8.5$ -9) upon evaporative concentration. As discussed in the following section, the abundance of Mg-silicates in presalt reservoirs strongly suggests that high concentrations of alkaline cations contributed to the chemical evolution of the presalt depositional system. By definition, these cations were not charge-balanced to any significant degree by  $\text{Cl}^-$  or any other salt-forming anion (Eqn. 1).

## 2.2 Mg-silicate minerals in carbonate sedimentary rocks

Although their global occurrence is relatively rare compared with the more common Al-rich clays, the authigenically precipitated, Al-poor, Mg-rich phyllosilicates, including sepiolite, stevensite, kerolite, and talc, collectively termed “Mg-silicates” here, can be abundant within sedimentary carbonates (Parry and Reeves, 1968; Gac et al., 1977; Tettendorf and Moore, 1978; Darragi and Tardy, 1987; Noack et al., 1989; Pozo and Casas, 1999; Terra et al., 2010; Guggenheim and Krekeler, 2011; Tosca et al., 2011; Bristow et al., 2012; Wright, 2012; Deocampo, 2015; Guggenheim, 2015; Tosca and Wright, 2015; Wright and Barnett, 2015;

Strauss et al., 2015; Pozo et al., 2016). In these rocks, Mg-silicates are variably associated with co-occurring carbonate minerals (i.e., calcite, aragonite, and dolomite) and detrital or authigenic Al-bearing clays, such that they may be trace or primary components. Mg-silicates appear as distinct, synsedimentary, nodular and void-filling phases (Tosca et al., 2011), discrete laminated or shale-like stratigraphic horizons (Terra et al., 2010; Tosca et al., 2011; Strauss et al., 2015; Saller et al., 2016), or disseminated amongst the co-occurring clay and carbonate phases of individual sedimentological units (Parry and Reeves, 1968; Terra et al., 2010; Wright and Barnett, 2015; Saller et al., 2016), with morphologies ranging from fibers or sheets filling the space between carbonate crystals (e.g., Wright and Barnett, 2015) to oolites surrounded by a carbonate/silica matrix (Tettenhorst and Moore, 1978; Noack et al., 1989). The major difference between the Mg-silicate occurrences in presalt rocks and these other occurrences is their scale: in the Barra Velha Formation, intervals over 150 m thick stretch for many kilometers (Wright and Barnett, 2015).

Guggenheim (2015), in a review of Mg-silicate crystal chemistry, discussed factors underlying their relative stabilities, in turn providing critical insight into precipitation kinetics. He notes that stevensite is in general a poorly defined, Al-free trioctahedral smectite, with an ideal chemical formula of:  $(M^{+}_{2y} \cdot nH_2O)(Mg_{3-y\Box})Si_4O_{10}(OH)_2$ , where  $M$  is the exchangeable cation in the interlayer (univalent here),  $\Box$  represents  $y$  vacancies, and  $n$  is variable. Importantly, this formula indicates that the chemistry of stevensite, including its Mg/Si ratio as well as the concentration of accessory cations such as Fe, K, Na, and Mn, can vary widely in response to variations in solution chemistry (e.g., Faust et al., 1959)—stevensite from Lake Yoa, for example, has the approximate formula:  $(Ca_{0.10}Na_{0.07}K_{0.09})(Mg_{2.79}Fe^{3+}_{0.02})Si_4O_{10}(OH)_2$  (Darragi and Tardy, 1987). Sepiolite, on the other hand, has a more rigorously defined chemical formula



(Mg<sub>8</sub>Si<sub>12</sub>O<sub>30</sub>(OH)<sub>4</sub>(OH<sub>2</sub>)<sub>3</sub>·8H<sub>2</sub>O) and tends to contain less than ~1 wt. % Na<sub>2</sub>O or K<sub>2</sub>O (Guggenheim, 2015), although the virtually crystallographically identical, Na-rich mineral loughlinite (Na<sub>4</sub>Mg<sub>6</sub>Si<sub>12</sub>O<sub>30</sub>(OH)<sub>4</sub>(OH<sub>2</sub>)<sub>3</sub>·8H<sub>2</sub>O) has been identified in the presalt-analogue Green River Formation in Wyoming (Fahey et al., 1960). Kerolite (Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·H<sub>2</sub>O), which is a low-temperature, hydrous form of talc, has also been identified in alkaline lake sediments (e.g., Pozo and Casas, 1999). By co-precipitating various Mg-silicates from aqueous solution at 25°C, Tosca and Masterson (2014) observed variable amounts of kerolite, stevensite, and sepiolite nucleation as a function of pH, Mg/Si and NaCl concentration. This highlights a strong kinetic control on nucleation and the role of ambient chemistry in the nature of the solid phase precipitated. Notably, the lowest Mg/Si ratio explored by Tosca and Masterson (2014) is greater (by a factor of 2) than what is likely to be characteristic of the alkaline lake systems generating presalt sediments.

Despite significant mineral chemical variability and kinetic controls on nucleation, clear boundaries for effective solubility of authigenic Mg-silicates have emerged from previous field and synthetic studies. For example, Darragi and Tardy (1987) used their analyses of Lake Yoa to determine an effective solubility ( $K_{apparent}$ ) for the end-member magnesian stevensite (Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>) as:

$$K_{apparent} = \frac{a_{Mg^{++}}^3 a_{SiO_2(aq)}^4 a_{H_2O}^4}{a_{H^+}^6} = 34, \quad (2)$$

where  $a$  designates the activity of the subscripted chemical species. To put this effective solubility in context, equation 2 implies that solutions must be many (i.e.,  $\geq 10$ -11) orders of magnitude supersaturated with respect to the Mg-silicates in order to spontaneously nucleate these phases. Importantly, compositional data show that the actual stevensite entering Lake Yoa

sediments contains significant quantities of  $\text{Fe}^{+++}$ ,  $\text{Ca}^{++}$ ,  $\text{K}^{+}$ , and  $\text{Na}^{+}$ , which indicates that this Mg-endmember solubility is relatively insensitive to the character of the other cations incorporated into the Mg-silicate structure. Indeed, in a series of more recent experimental studies (Tosca et al., 2011; Tosca and Masterson, 2014; Tosca, 2015), this effective solubility has been shown to be generally applicable to other Mg-silicates, including kerolite and sepiolite.

### **2.3 Silica in alkaline lakes**

Silica, in the form of syndepositional and diagenetic chert, represents a labile component of the presalt depositional system (Wright & Barnett, 2015; Saller et al., 2016), yet the processes that control  $\text{SiO}_2$  concentrations during alkaline chemical sedimentation are not well understood. During evaporation of alkaline lakes,  $\text{SiO}_2$  concentrations will be principally controlled by: (1) solubility constraints applied by amorphous silica saturation, (2) silica uptake by mineral surfaces, and (3) the precipitation of Mg-silicates. Siever and Woodford (1973), Hager (1980), and Siever (1992) have all emphasized the diagenetic implications of silica sorption onto clay minerals and carbonates in marine settings, processes which are also applicable to alkaline lakes. Nonetheless, relatively few measurements of silica uptake onto Mg-silicates and  $\text{CaCO}_3$  have been performed in general, and none seem to have been performed at pH and  $\text{SiO}_2$  concentrations relevant to alkaline lakes, thus limiting the extent to which these data can be used to interpret and predict  $\text{SiO}_2$  dynamics in the presalt depositional environment.

### **2.3 Observational constraints on presalt deposition**

In addition to the geochemical considerations discussed above, published mineralogical and petrographic data of presalt rocks provide additional constraints on chemical processes responsible for their formation. For example, the mere abundance of authigenically precipitated

Mg-silicates (e.g., Wright and Barnett, 2015) strongly implicates elevated pH conditions, at least ~9 or above (Tosca et al., 2011) within the paleolake waters. Similarly, the spherulitic morphology of  $\text{CaCO}_3$  associated with Mg-silicates in presalt core samples (Fig. 1) is also indicative of elevated pH in the range of ~10-10.5 (Garcia-Ruiz 1998). Together, these combined mineralogical constraints indicate that the lake that formed the spherulitic facies in the presalt carbonates had an initial  $[\text{Ca}^{++}]/[\text{Alkalinity}]$  ratio considerably less than 0.5 with a high concentration of alkalinity-balancing cations (Eqn. 1) and an evaporation-induced, steady-state pH of ~10-10.5. The abundance of Mg-silicates also suggests elevated dissolved  $\text{SiO}_2$  concentrations as well as abundant dissolved  $\text{Mg}^{++}$ . Nonetheless, apart from some relatively coarse inferences based upon the igneous/metamorphic rocks inferred to have been the watershed for the presalt lakes, little is known about how the concentrations of cations other than  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  may have influenced the deposition of the presalt carbonates, and, moreover, the coupled processes of Mg-silicate and  $\text{CaCO}_3$  growth are not well understood.

In this experimental study, we use these inference-based constraints as a foundation to quantify the processes, mechanisms, and rates of Mg-silicate-bearing lacustrine reservoir rock formation. We explore the effects of: 1) the differing relative concentrations of  $\text{Mg}^{++}$  and  $\text{Ca}^{++}$ ; 2) the dominant alkalinity-producing cation ( $\text{K}^+$  vs.  $\text{Na}^+$ ), and 3) mineral substrate-controlled growth relevant to detrital zones of the lake, re-working episodes, and/or processes below the sediment-water interface. Using real-time observations of *in situ* fluid chemistry, post-experiment analysis of solid precipitate chemistry and mineralogy, and a thermodynamics- and kinetics-based geochemical modeling framework, we produce a uniquely complete set of observations which will help to contextualize, interpret, and predict the geochemical behavior of presalt and other lacustrine carbonate reservoirs.

### 3. Methods

#### 3.1 Experimental design

In order to provide quantitative laboratory constraints on the interactions between Mg-silicates and carbonates during growth from silica-rich, alkaline lakes, we performed a suite of experiments in simulated lake solutions at a range of initial Mg and Ca concentrations with and without initial seed minerals. These twelve experiments are henceforth referred to as “mineral precipitation experiments.” Synthetic lake waters were prepared by adding reagent-grade  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{K}_2\text{CO}_3$  and/or  $\text{KHCO}_3$  to nanopure (18 M $\Omega$ ) deionized water. All experiments were performed with solutions having an *in situ* pH  $\approx$  10.2, which, in keeping with the simulated alkaline lake water, was buffered by alkalinity and atmospheric partial pressure of carbon dioxide ( $\sim 10^{-3.5}$  atm) using calculated additions of either the  $\text{Na}_2\text{CO}_3$ - $\text{NaHCO}_3$  or  $\text{K}_2\text{CO}_3$ - $\text{KHCO}_3$  buffers (Table 1). This pH was chosen to approximate the expected steady-state pH of evaporatively concentrated alkaline lakes, although natural systems generally have a mixture of  $\text{Na}^+$ ,  $\text{K}^+$ , and other cations and anions accounting for their overall alkalinity budget and hence pH. Although modern atmospheric  $p_{\text{CO}_2}$  is lower than that representative of the Cretaceous atmosphere (e.g., Hönisch et al., 2012), this difference negligibly affects our results, because inorganic carbon within the simulated lake waters is in considerable excess at this pH, regardless of differences in  $p_{\text{CO}_2}$ .

Because this pH is above the ambient-temperature pK for silicic acid (9.95), amorphous silica is much more soluble than at lower pH ( $\sim 6.5$  mmol/kg at pH = 10.1 and alkaline lake ionic strength of 0.55 compared to  $\sim 1.8$  mmol/kg at 21°C pH=7 (Gunnarsson and Arnórsson, 2000)). Importantly, calculations of amorphous silica solubility at this high pH are abnormally sensitive to the solution ionic strength (Zarubin and Nemkina, 1990) due to the charged species  $\text{HSiO}_3^-$

being the dominant silica species and are thus more uncertain than calculations performed at lower pH.

After the initial addition of the  $\text{Na}_2\text{CO}_3$ - $\text{NaHCO}_3$  or  $\text{K}_2\text{CO}_3$ - $\text{KHCO}_3$  solids to the solution, buffer solutions were mixed while in contact with the atmosphere for at least one day in order to permit any minor  $\text{CO}_2$  uptake or efflux required to equilibrate with atmospheric  $\text{pCO}_2$ . To achieve  $\text{SiO}_2$  concentrations near amorphous silica saturation, silica was then added to the atmospherically-equilibrated solution in the form of tetraethyl orthosilicate (TEOS- used in experiments A-C only) or sodium metasilicate nonahydrate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ), and then allowed to equilibrate for at least an additional day. TEOS has been used in many previous experimental studies of Mg-silicate growth (e.g., Tosca et al., 2011; Tosca and Masterson, 2014), but it was determined to be considerably easier to reach the high  $\text{SiO}_2$  concentrations utilized in this study with sodium metasilicate nonahydrate as the Si source. Lastly, initial Mg and Ca concentrations were achieved just prior to experiment initiation by first diluting 1 M  $\text{MgCl}_2$  and  $\text{CaCl}_2$  5-10 times with nanopure water to make up a 10 mL volume and then slowly adding them to the alkaline silica solution while mixing.

Four experiments were performed using powdered mineral seeds in order to examine the effects of pore-water growth and/or detritus-seeded growth on alkaline lake chemistry. Two of these experiments (experiments E and F) contained 0.1 g of natural sepiolite ( $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ , Brunauer-Emmett-Teller specific surface area (BET SSA (Brunauer et al., 1938) =  $252 \text{ m}^2/\text{g}$ ) purchased from Sigma-Aldrich<sup>®</sup> and two of these experiments (G and H) contained 0.1 g of high purity laboratory reagent grade gibbsite ( $\text{Al}(\text{OH})_3$ , BET SSA =  $0.93 \text{ m}^2/\text{g}$ ) from Fisher Scientific Ltd. This 0.1:1000 mass ratio between the seed material and the solution was chosen to minimize the effect of sorption processes on measured aqueous  $\text{SiO}_2$

concentrations while still providing a realistic substrate concentration to test its effects on growth.

Expts. A-C were performed in 1 L narrow mouth polycarbonate (PC) bottles, whereas experiments D-L were performed in 1 L wide mouth low density polyethylene (LDPE) bottles. The decision was made to switch from the clear PC to the translucent LDPE bottles after the initial three experiments because of the difficulty in extracting precipitated material from the narrow-mouth PC bottles post-experiment. PC bottles have been used in many previous experiments examining carbonate precipitation (e.g., Land, 1998), and we can thus confirm that the difference in bottle material should not have affected solution chemistry. Notably, limited quantities of solids were recovered from experiments B and C, which also had comparatively low initial Mg and Ca concentrations and hence would not be expected to have yielded much material regardless of the recovery issues. Experimental bottles were mixed using an orbital shaker at ambient laboratory conditions (21°C) and remained sealed throughout the duration of the experiment, except for the 1-2 minute intervals during which samples were acquired.

An additional set of twelve experiments (including one blank) was performed to examine the uptake of silica by the minerals sepiolite, gibbsite, calcite, and talc in the absence of Mg or Ca from the  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  buffered solution at pH 10.2 using a similar approach to that described by Siever and Woodford (1973) for aluminous clays. These experiments are henceforth referred to as “silica uptake experiments.” The sepiolite and gibbsite were from the same stock as those used in the lake analogue experiments, the calcite was a 98+% purity synthetic powder from Acros Organics (BET SSA =  $1.19 \text{ m}^2/\text{g}$ ), and the talc was a natural powder obtained from Fisher Scientific, sieved to retain the 45-90  $\mu\text{m}$  solid fraction and sonicated to remove ultrafine particles (BET SSA =  $1.81 \text{ m}^2/\text{g}$ ). Solutions were prepared

identically to the stock solutions for the experiments above, using  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  as the silica source, and added to 60 mL LDPE bottles along with varying amounts of the mineral of interest (Table 2). This set of experiments was run for a total of 94 days, and solution chemistry samples were obtained at 12, 35, and 94 days in order to monitor the amount of  $\text{SiO}_2$  in solution and to confirm the constancy of pH.

In these experiments, surface area-normalized silica uptake was calculated by fitting a line to plots of Si uptake versus mineral surface area for the three (two, in the case of talc) individual experiments for a particular mineral substrate. Note that the final, 94-day sample for the 60 mL blank experiment was inadvertently spilled during preservation; however the two previous samples indicated no silica removal within the error of the measurements, and 1-L LDPE bottles containing the  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  and  $\text{KHCO}_3$ - $\text{K}_2\text{CO}_3$  buffers with 6 mmol/kg Si showed no silica depletion, within error, after 129 and 58 days, respectively. We thus conclude that Si depletion did not occur as an artifact of the experimental procedure, as discussed below.

### **3.2 Analytical procedures**

Fluid samples (1-1.5 mL) were taken periodically throughout the experiments and filtered through 0.22  $\mu\text{m}$  Durapore<sup>®</sup> PVDF syringe filters. An aliquot of these samples was preserved and diluted at least 6 times with 4% analytical reagent grade nitric acid in order to prevent mineral precipitation during storage. In addition, pH was measured on 0.5 – 1.0 mL samples using a Thermo Scientific<sup>™</sup> Orion<sup>™</sup> 8103BN ROSS<sup>™</sup> Combination Semi-micro pH Electrode, which was calibrated at least daily using NIST-traceable pH 7 and 10 buffers. Concentrations of dissolved Na, K, Ca, Mg, and Si were measured using a Perkin Elmer Optima 7300 DV Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) at the Scottish Universities Environmental Research Centre (SUERC) in Glasgow, Scotland, United Kingdom.

Individual samples were analyzed in triplicate, and the standard deviation for all samples included in Table 3 are less than 5%, except for several Ca samples with concentrations under 10  $\mu\text{mol/kg}$ , for which the standard deviation ranged up to  $\sim 9\%$ . Measurements of Na and K in  $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$  and  $\text{K}_2\text{CO}_3\text{-KHCO}_3$  solutions, respectively, are accompanied by additional uncertainty due to the high dilution required for analysis and hence were screened to remove clearly unreasonable measurements (these were replaced in Table 3 by the concentration calculated from the added reagents, which is more accurate). Measurements were additionally left out of Table 3 if they were considerably out of trend (i.e.,  $\geq 10\%$ ) with the surrounding two measurements. A certified groundwater reference sample (CRM ESH-2, ESH-3) was analyzed alongside the samples reported in Table 3 in order to monitor instrument precision and ensure reliability. Due to the specific intentions for the set of 60 mL silica uptake experiments, these solutions (which were preserved identically to those obtained from the lake-analogue experiments) were analyzed for silica concentration according to the molybdate blue method with metol as the reducing agent (Mullin and Riley, 1955) by measuring absorbances at a wavelength of 812 nm using a HACH spectrophotometer calibrated with sample-bracketing standards of known composition. The calibration line reproduced the standard concentrations with an accuracy better than 2%.

After experiment termination, solid precipitates were vacuum-filtered onto 0.22  $\mu\text{m}$  Durapore<sup>®</sup> filters, rinsed with at least 500 mL of deionized water, and dried in air in a natural convection oven at 60°C. These collected materials were characterized using X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) imaging coupled to energy dispersive x-ray spectroscopy (EDS) for chemical analyses. XRD measurements were performed between 5 and 80 degrees ( $2\theta$ ) on solids



deposited as a slurry and dried onto spinning, zero-background silicon stages using a PANalytical Empyrean outfitted with a Co K $\alpha$  X-ray source. B.E.T. (Brunauer et al., 1938) 5-point N<sub>2</sub> sorption surface areas were acquired for mineral substrates on a Micromeritics Gemini V2.0 at the Begbroke Science Park at the University of Oxford. FTIR spectra were acquired over the wave number range from 400 cm<sup>-1</sup> to 4000 or 8000 cm<sup>-1</sup> in transmission mode on optically translucent disks, which were prepared by grinding ~2 mg of sample into 200 mg of dried (at 150°C) KBr powder, and then compressing the mixture under vacuum in a hydraulic press. Finally, samples were prepared for SEM analyses by adhering gently disaggregated solids to conductive carbon tape and sputter coating with Au-Pd. SEM imaging and measurements were performed at 10 kV accelerating voltage with a 3  $\mu$ m spot size using a FEI Quanta 650 Field Emission Gun instrument in high vacuum mode. In order to provide a meaningful basis for comparison across samples, each EDS spectrum was analyzed identically for the Na, K, Ca, Mg, O, and Si lines (i.e., H and the Au-Pd coating were excluded from the sum) and normalized to 100%.

### 3.3 Geochemical calculations

Geochemical calculations were performed using the Geochemist's Workbench (GWB, Bethke and Yeakel, 2015) with a database custom-made for the present study with the DBCreate software package (Kong et al., 2013) (included in supporting online information). The major changes between this database and those which are included with the GWB installation are as follows: 1) revised thermodynamic properties for SiO<sub>2</sub>(aq) presented by Sverjensky et al. (2014), which are consistent with revised low-temperature quartz and amorphous silica solubilities presented by Rimstidt (1997) and Gunnarsson and Arnórsson (2000), respectively; 2) thermodynamic properties of amorphous silica were reverted to those presented by Robie et al.

(1978) which are consistent with Gunnarsson and Arnórsson (2000); and 3) the  $\text{NaHSiO}_3(\text{aq})$  complex, whose stability was originally questioned by Busey and Mesmer (1977) on the basis of inaccurate pH constraints in the original experimental study presented by Seward (1974), was removed from the database. A comparison between the predicted solubility of amorphous silica in Na-rich solutions using our thermodynamic database and literature solubility determinations is illustrated in Fig. 2. The updated database offers dramatically improved agreement with the experimentally measured values in comparison to currently existing data sources, especially whenever the  $\text{NaHSiO}_3(\text{aq})$  complex is included in the latter. This agreement can be improved somewhat at  $\text{pH} \gtrsim 10.5$  if higher-order silica species are included in the database (Felmy et al., 2001), but these species were not considered both because all experiments discussed here were performed at  $\text{pH} \approx 10.2$  and also because, at this high pH, charge balance dictates that solution ionic strength is increasingly out of the field of applicability of the activity model used here. A further testament to this database's utility in interpreting our experimental results is demonstrated in Table 1, which shows good agreement between the calculated and measured values of the synthetic lake water pH. All speciation calculations utilize the extended "B-dot" Debye-Hückel equation (Helgeson, 1969) for charged species activity coefficients. Neutral species were assumed to have activity coefficients of unity, which should introduce negligible additional uncertainty at our ionic strength conditions (Garrels and Christ, 1965). The saturation ( $\Omega$ ) of Mg-silicates were calculated utilizing this speciation model according to:

$$\Omega = \frac{Q}{K} \quad (3)$$

where  $Q$  is the ion activity product and  $K$  is the equilibrium constant, or, as discussed above, the apparent Mg-silicate solubility defined by Eqn. 2.

## 4. Results

### 4.1 Fluid Chemistry

#### 4.1.1 Mineral precipitation experiments

Time-series measurements of solution chemistry illustrate the varying timescales over which mineral growth and/or element sorption affect the concentration of various species in solution (Table 3). The concentrations of Ca, Mg, and Si in solution generally decreased with time in all experiments (Figs. 3 and 4, Table 3), and, while Ca depletions in solution tend to show no relationship with either Mg or Si concentrations (Table 3), the magnitude of the total  $\text{SiO}_2$  decrease generally correlates with the initial Mg concentration (Table 3, Fig. 4). The total amounts of Mg and Si depletion in the  $\text{KHCO}_3$ - $\text{K}_2\text{CO}_3$  buffered experiments tend to be systematically lower than those from the  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  experiments, even though they were run for similar durations. When plotting Mg concentrations versus  $\text{SiO}_2(\text{aq})$  concentrations, all experiments—except for Expt. B, which started with an initial Mg concentration of 0.1 mmol/kg and has a slope of effectively 0—can be described within the error of the measurements with a line of constant slope (Fig. 4). In all experiments, the slopes of the Mg vs. Si solution chemistry measurements tend to be in good agreement with the measured Mg/Si ratio of the recovered products (by SEM-EDS spot analyses), which, notably, also contain significant amounts of Na and K (Table 4).

Ca decreased rapidly in experiments with initial Ca concentrations of 0.5 mmol/kg or above, such that concentrations of  $\sim 0.1$  mmol/kg or below were achieved within about one week of the start of these experiments (Fig. 3). On the other hand, experiments with starting Ca concentrations of 0.1 mmol/kg showed a variety of behaviors. Of these, Expt. F, which contained 0.1 g of sepiolite, showed the most dramatic reductions in Ca concentration, such that

its concentration after 50 days was  $\sim 20 \mu\text{mol/kg}$ . Concentrations of Ca in experiment H, on the other hand, remained virtually unchanged throughout the experiment, in spite of the fact that it contained 0.1 g of gibbsite seed material. For comparison, Expt. C, which was initialized with a similar Ca concentration and contained no mineral seed, showed consistently decreasing Ca concentrations during the first 24 days and leveled off at a concentration of  $\sim 50 \mu\text{mol/kg}$  during the final 13 days before experiment termination. At these conditions, the thermodynamic solubility of calcite and aragonite are limited to under  $1 \mu\text{mol/kg}$ , so all experiments were strongly supersaturated with respect to these minerals, in spite of their relatively low concentrations.

#### **4.1.2 Silica uptake experiments**

The results of the silica uptake experiments are presented along with the experimentally varied parameters in Table 2. Fits to the plots of mineral specific surface area or mass versus silica uptake measured after 94 days yield values ranging from  $6.5 \times 10^{-4} \text{ mmol/m}^2$  (for sepiolite) to  $5.7 \times 10^{-2} \text{ mmol/m}^2$  (for calcite), and from 0.067 mmol/g (for calcite) to 0.17 mmol/g (for sepiolite), and hence show different behavior relative to one another depending on whether they are normalized by surface area or mass. In contrast to the experiments that were run without added mineral substrates, which showed immeasurable amounts of silica depletion, these fitted lines yield non-zero values of Si uptake at zero mineral mass for all experiments, ranging from 4  $\mu\text{mol}$  in the case of gibbsite to 23  $\mu\text{mol SiO}_2$  in the case of sepiolite. A change of this magnitude would, notably, be below the detection limits for silica concentrations in the mineral precipitation experiments.

### **4.2 Solid Chemistry and Morphology**

#### **4.2.1 X-ray Diffraction Results**

XRD patterns allow for crystallographic identification of minerals precipitated during the lake analogue experiments (Fig. 5,6; Table 5).  $\text{CaCO}_3$  was identified in XRD patterns for all experiments which were initialized with Ca in solution (i.e., all experiments except D and J). Expts. B and C yielded insufficient solid for XRD measurements, as did experiment H, whose XRD pattern was dominated by that of the gibbsite mineral seed. Both aragonite and calcite are present in XRD data, except for Expts. F, I, and L, which appear to contain  $\text{CaCO}_3$  only as aragonite. Broad XRD peaks consistent with layer silicate minerals are additionally present in all experiments for which data are available, except again for Expt. H, which, within the limits of the XRD measurements, appears to contain only gibbsite. The positions of these peaks are generally consistent from sample to sample and include peaks indicative of low angle basal reflections (between 14-15 Å and at ~12-12.5 Å), and also broad peaks at ~6.8, 4.3, 2.6, and 1.52-1.53 (Fig. 5). These latter peaks originate from overlapping *hkl* reflections and peak broadening produced from very small coherent scattering domain size (i.e., tens to hundreds of nanometers (Moore and Reynolds, 1997)). The presence of these peaks indicates the development of layered (and modulated) silicate structures, in particular the low-angle basal peaks and the composite “060” reflection at 1.52-1.53 Å, the latter of which indicates the development of a trioctahedral layer (Moore and Reynolds, 1997).

Although the low-angle peaks are diffuse, attempts to deconvolve the peaks from the mineral-free background allow for examination of the apparent d-spacing of the precipitated Mg-silicate phases (Fig. 6). Solids recovered from the  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  buffered experiments tend to have sharper and more distinct peaks than those recovered from the  $\text{KHCO}_3$ - $\text{K}_2\text{CO}_3$  buffered experiments. The apparent d-spacing (~13.6 Å) changes relatively little as a function of the experimental conditions, but, in detail, reflects varying contributions of multiple phases (Fig. 6).

These include mixtures of (1) the crystalline Mg-silicates sepiolite (12.1 Å), loughlinite (12.85 Å) and (2) stevensite (with reports varying between 13.5-15.5 Å). Fig. 5, for example, shows powder diffraction data for three experiments (A, D and I) at increasing Mg/Si. Low angle reflections show increasing contributions of sepiolite/loughlinite (apparent d-spacing at ~12.2 Å) at low Mg/Si, in addition to the presence of a phase with consistent apparent d-spacing of ~14-14.7 Å, which we identify as stevensite. Stevensite is known to display complex diffraction behavior as a function of relative humidity and air dried treatment, with apparent d-spacings in the air-dried state ranging from ~13 to 15 Å (Shimoda, 1971; Guggenheim, 2015). This is most likely a function of two layer types present within stevensite (hydrated and dehydrated) which variably contribute to apparent d-spacing measurements, and offers a reasonable explanation for the variability we observe here (Faust et al., 1959; Shimoda, 1971; Guggenheim, 2015). Interestingly, a broad peak centered at 13-14 Å is present in Expt. G, which was initialized with gibbsite seed material, suggesting that Mg-silicates were able to nucleate and grow in the presence of gibbsite.

#### **4.2.2 Fourier Transform Infrared Spectroscopy Results**

FTIR spectra provide a more nuanced description of the precipitates formed in the lake analogue experiments (Fig. 7). Consistent with powder X-ray diffraction data, FT-IR spectra clearly show the contribution of CaCO<sub>3</sub> phases in addition to Mg-silicate phases. Dominant CaCO<sub>3</sub> absorptions (arising from both calcite and aragonite) include an intense doublet at ~1450-1500 cm<sup>-1</sup>, which arises from the ν<sub>3</sub> asymmetrical CO<sub>3</sub> absorption, as well as sharp features at ~870-880 and 714 cm<sup>-1</sup>, corresponding to ν<sub>2</sub> and ν<sub>4</sub> CO<sub>3</sub> absorptions, respectively (Fig. 7, (Farmer, 1974; Russell and Fraser, 1994)).

Features that arise in the lattice vibration portion of the FT-IR spectrum can be used to distinguish Mg-silicates precipitated in the experiments. For example, Fig. 7 shows FT-IR spectra from experiments A, D, and I, which corresponds to powder X-ray diffraction data from the same experiments shown in Fig. 5. The lattice vibration region shows strong absorptions at 480, 680, and 1010-1020  $\text{cm}^{-1}$ ; these are consistent with Mg-silicate structures (Tosca et al., 2011; Tosca & Masterson, 2014). The latter feature arises from the Si-O stretch present in 2:1 layer silicate structures such as stevensite (Farmer, 1974; Russell & Fraser, 1994; Tosca et al., 2011; Tosca & Masterson, 2014). In addition, Expt. A clearly shows the presence of a shoulder positioned at  $\sim 1200 \text{ cm}^{-1}$  (Fig. 7); this absorption is diagnostic of Si-O-Si stretching from inverted silica tetrahedra in modulated layer silicates such as sepiolite or loughlinite (Russell & Fraser, 1994; Tosca & Masterson, 2014). Consistent with powder X-ray diffraction data from the same samples (Fig. 5), the intensity of this absorption progressively decreases with increasing Mg/Si, reflecting increasing dominance of neoformed Mg-silicates by stevensite as opposed to loughlinite-sepiolite. In addition, the hydroxyl stretching region of the FT-IR spectrum shows a sharp absorption at 3690  $\text{cm}^{-1}$ , which arises from  $\text{Mg}_3\text{-OH}$  stretching in trioctahedral domains or layers, confirming the Mg-rich nature of the layer silicates (Russell & Fraser, 1994; Tosca & Masterson, 2014). Other absorptions, notably the 3390, 3480, and 3630, indicate complex and variable hydration in both stevensite and sepiolite-loughlinite. In summary, FT-IR data are consistent with XRD data that show the presence of both stevensite and sepiolite-loughlinite (in addition to  $\text{CaCO}_3$  phases), and their relative proportion is clearly sensitive to subtle changes in solution chemistry.

#### **4.2.3 Scanning Electron Microscopy Results**

SEM images (Fig. 8) and coupled EDS analyses (Table 4) provide additional constraints on the morphological and chemical makeup of the experimental precipitates. In all experiments in which solution chemistry changes indicate appreciable  $\text{CaCO}_3$  precipitation (Fig. 3, Table 3),  $\text{CaCO}_3$  with spherulitic morphology was identified visually (Fig. 8) or with EDS field-of-view chemical analyses (Expts. E and F). Expt. B, which was initialized with the lowest Mg concentration (0.1 mmol/kg) is the only experiment in which both non-spherulitic and spherulitic  $\text{CaCO}_3$  were observed. No  $\text{CaCO}_3$  spherules were identified in the gibbsite-seeded Expt. H, which fluid chemistry data (Table 3, Fig. 3) confirm was the only experiment that, despite initial supersaturation with respect to  $\text{CaCO}_3$ , did not precipitate appreciable quantities of either calcite or aragonite.

In every experiment where Mg-silicates and carbonates have been identified (by XRD and/or FT-IR), Mg-silicates surround spherulitic  $\text{CaCO}_3$  (Fig. 8). The average atomic ratio of cations to silica (i.e.,  $(\sum \text{Cation}/\text{Si} = 0.5(\text{Na} + \text{K}) + \text{Mg})/\text{Si}$ ) in all Mg-silicates recovered from all experiments is  $\sim 0.46$ . The Mg-silicates precipitated in the  $\text{KHCO}_3$ - $\text{K}_2\text{CO}_3$  experiments tend to be comparatively Si-rich (average  $\text{Mg}/\text{Si} = 0.41$ ) with lower  $\sum \text{cation}/\text{Si}$  ratios (average = 0.46) than the analogous values acquired for those precipitated in the  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$ -buffered experiments (average  $\text{Mg}/\text{Si} = 0.51$ , average  $\sum \text{Cation}/\text{Si} = 0.56$ ). Collectively, these EDS analyses (Table 4) are in good agreement with the changes in Mg and Si observed within the solution chemistry (Fig. 4). In general, these numbers are lower than those for any known Mg-silicate (sepiolite/loughlinite, with a  $\sum \text{Cation}/\text{Si}$  of 0.67 is the closest in resemblance), suggesting that excess Si is taken up by the solids during the experiments, a process which we discuss in more detail below. Although their compositional ranges overlap, it appears that solutions with initial  $\text{Mg}/\text{Si}$  ratios of 2/6 tend to have higher  $\text{Mg}/\text{Si}$  and  $\sum \text{Cation}/\text{Si}$  values than those with



initial Mg/Si of 1/6. EDS atomic ratios indicate that the Mg-silicates contain Na in experiments which were buffered by the  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  buffer and both Na and K in experiments which were buffered by the  $\text{KHCO}_3$ - $\text{K}_2\text{CO}_3$  buffer (note that, due to the silica source ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ), these solutions initially contained  $\sim 12$  mmol/kg Na (Table 2)).

## **5. Discussion**

### **5.1 Interplays between solution chemistry and mineral growth**

The evolution of fluid and solid chemistry during our experiments permits quantitative descriptions of the simultaneous nucleation and growth of  $\text{CaCO}_3$  and Mg-silicate minerals from alkaline lakes during evaporative concentration. The timescales over which  $\text{CaCO}_3$  grows and the degree to which its solubility is governed by thermodynamic equilibrium are considerably shorter and greater, respectively, than the equivalent processes for Mg-silicates. Furthermore, the nature of the alkalinity-generating cations in solution has a pronounced effect on the chemical properties of the precipitated Mg-silicate phase, with surprising implications for the stoichiometric evolution of Mg and Si in these solutions. The auxiliary sorption experiments run without Mg or Ca provide additional insights into the processes contributing to silica behavior during the authigenic phase of lacustrine carbonate reservoir formation. In this section, we first discuss the control that  $\text{CaCO}_3$  and Mg-silicate solubilities play upon solution chemistry and mineral precipitation processes. Subsequently, we utilize kinetic theory to explain the apparent solubility of Mg-silicates as derived from our experimental data. Finally, based on these results, we present a conceptual model for how evaporation might have influenced the deposition of Mg-silicate and carbonate-rich facies of the presalt reservoirs.

#### **5.1.1 $\text{CaCO}_3$**

A key first-order observation of our time-series fluid chemistry data (Fig. 3, Table 3) is that the timescales over which  $\text{CaCO}_3$  nucleates and grows from solution are significantly shorter than those for the Mg-silicates, even though the latter are many orders of magnitude more supersaturated. Elevated concentrations of dissolved silica have previously been shown to decrease the induction time for  $\text{CaCO}_3$  nucleation without affecting the identity of the precipitated  $\text{CaCO}_3$  phase (Lakshtanov and Stipp, 2010), which suggests that  $\text{SiO}_2$  can serve to stabilize  $\text{CaCO}_3$  nuclei. As illustrated in Fig. 3, an initial Ca concentration of  $\sim 0.5$  mmol/kg (i.e., a  $\text{CaCO}_3$  supersaturation of  $\sim 10^{1.7}$ ) homogeneously nucleates enough  $\text{CaCO}_3$  to then promote sustained growth and remove much of the Ca from solution. It hence seems unlikely that Ca concentrations  $\geq 0.1$  mmol/kg could be sustained for any length of time within the alkaline lake settings that are the focus of this study, and the concentrations may have been considerably lower than that.

As our experimental data additionally illustrate, the difference in the growth timescales for Mg-silicates and  $\text{CaCO}_3$  has interesting implications for the nature of the precipitated  $\text{CaCO}_3$  phase due to the control that solution Mg/Ca places on the relative proportions of calcite and aragonite that are precipitated. Relatively low and high Mg/Ca ratios tend to favor the production of calcite and aragonite, respectively, from seawater (e.g., Balthasar and Cusack, 2014), and recent observations have confirmed that a threshold of  $\text{Mg/Ca} \approx 1.1$  separates these two predominance fields for continental waters with lower Mg and Ca concentrations (Rossi and Lozano, 2016). These previous studies suggest that the measured increases in the Mg/Ca of our experimental solutions with time (Table 3) would have driven a transition from  $\text{CaCO}_3$  precipitation as calcite at low Mg/Ca to aragonite at high Mg/Ca as the solution chemistry evolved in those experiments initialized with Mg/Ca less than 1.1, and that those initialized with

593 Mg/Ca greater than 1.1 would have precipitated  $\text{CaCO}_3$  as aragonite only. Indeed, aragonite  
594 appears to be the sole  $\text{CaCO}_3$  mineral precipitated in Expts. F, I, and L, which had initial Mg : Ca  
595 ratios of 0.5 : 0.1, 2 : 1, and 2 : 1 (all mmol/kg : mmol / kg), and all experiments initialized with  
596 Mg/Ca of 1 mmol/kg : 1 mmol/kg (i.e., Expts. A, E, G, and K) appear to have precipitated both  
597 calcite and aragonite. Presumably, calcite precipitated during the initial hours or days of these  
598 experiments and gave way to aragonite precipitation quite rapidly, as Ca was mostly depleted  
599 from the majority of these solutions by the time the second sample had been taken.

600 Wright and Barnett (2015) suggest that spherulitic  $\text{CaCO}_3$  in presalt carbonates was  
601 precipitated as calcite, and further, that spherulitic calcite growth is influenced or enhanced by  
602 the presence of incipient Mg-silicate precipitates. Mercedes-Martín et al. (2016) tested the  
603 hypothesis that Mg-silicates contribute to the spherulitic morphology of  $\text{CaCO}_3$  in alkaline lake  
604 sediments, and additionally examined the role that organic acids may play on the growth of  
605 spherulitic carbonates. Their conclusions suggest that Mg-silicate gels are not required to  
606 precipitate spherulitic  $\text{CaCO}_3$ , but rather that the presence of certain environmentally relevant  
607 organic acids facilitate spherulite growth. In contradiction to these results, our experiments  
608 suggest little to no influence of organic molecules on the precipitation of spherulitic  $\text{CaCO}_3$ ,  
609 because, apart from experiments A-C, which contained ethanol as a byproduct of TEOS addition,  
610 our experiments repeatedly precipitated spheroidal  $\text{CaCO}_3$  in the absence of organic molecules,  
611 both with (Fig. 8 A,E,G,I-J) and without (Fig. 8 B-C) simultaneous Mg-silicate precipitation,  
612 including in the presence of crystalline gibbsite (Fig. 8E). Together, our experimental  
613 observations confirm inferences based on the previous experimental results of Garcia-Ruiz  
614 (1998), who showed that silica-rich, alkaline lakes buffered at  $\text{pH} \approx 10.2$  precipitate spheroidal  
615 carbonates. It is possible that variations in  $\text{CaCO}_3$  morphology observed by Mercedes-Martín et

al. (2016) were more closely associated with the pH variation during their apparently unbuffered experiments. Their experiments achieved final pH values of 6.7-8.2 from initial values of 10-11, likely due to acidity production during carbonate precipitation. It is also possible that comparatively low  $\text{SiO}_2$  concentrations in their experiments ( $\sim 0.6$  mmol/kg vs.  $\sim 6$  mmol/kg in this study) could have influenced their results.

The major  $\text{CaCO}_3$  mineral precipitated in our experiments is aragonite, although the fact that many experiments appear to contain both aragonite and calcite (Sect. 4.2) makes it difficult to unambiguously discern whether the spheroidal  $\text{CaCO}_3$  is mineralogically calcite or aragonite. XRD measurements indicate that Expts. I and L contain  $\text{CaCO}_3$  solely as aragonite. These data, in addition to SEM evidence showing that the carbonate produced in these experiments is spheroidal (Fig. 8 G,J) suggests that aragonite can indeed precipitate as spheroids. This result thus implies that the interfacial processes that give rise to the unique  $\text{CaCO}_3$  morphologies in alkaline,  $\text{SiO}_2$ -rich solutions are more influential than the identity of the precipitating mineral (indeed, the experiments performed by Garcia-Ruiz (1998) utilized  $\text{BaCO}_3$  and  $\text{SrCO}_3$  and not  $\text{CaCO}_3$ ), but a focused study buffered at conditions similar to those used in this study at a broader range of initial Ca concentrations and Mg/Ca ratios will be required in order to conclusively determine this effect.

### **5.1.2 Mg-silicates**

Both the initial Mg concentration and the identity of the alkalinity-producing cation play a clear role in controlling the amount of Mg-silicate precipitated during our experiments. Of these controls, most unexpected was that  $\text{Na}^+$  apparently plays a key role in facilitating Mg-silicate growth. Every  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$ -buffered experiment which was initially critically

supersaturated with respect to Mg-silicate (defined by Eqn. 2) either very nearly reached that critical supersaturation or dropped below it by the time the experiment was terminated, while none of the  $\text{KHCO}_3$ - $\text{K}_2\text{CO}_3$ -buffered experiments did (Fig. 9). Furthermore, in the  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$ -buffered experiments, the apparent rates of Mg-silicate nucleation and growth stayed constant, even as the more highly supersaturated solutions (e.g., Expts. A, D, E, G, and I) became less supersaturated than the others (e.g., Expts. B, C, F, H). The results of Expt. B provide an important baseline for interpreting the other experiments, since this experiment plots below the critical supersaturation and measured Mg concentrations confirm that this experiment precipitated no Mg-silicates. The fact that the Mg-silicates precipitating in Expts. D, E, G, and I continued to grow after passing below the supersaturation calculated for Expt. B is, thus, particularly notable, since this behavior confirms that homogeneous nucleation is favored above the critical supersaturation defined by Eqn. 2 and that heterogeneous growth of Mg-silicate can continue to deplete solution Mg and Si provided that the solution remains in contact with the mineral nuclei. We explore the energetics of this process in more detail below.

Experiments run with the  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  buffer precipitated comparatively more Mg-silicates than experiments run with the  $\text{KHCO}_3$ - $\text{K}_2\text{CO}_3$  buffer. Mg-silicates precipitated in the  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  buffered experiments contained  $\text{Na}^+$ , while those precipitated in the  $\text{KHCO}_3$ - $\text{K}_2\text{CO}_3$  buffered experiments contained both  $\text{Na}^+$  and  $\text{K}^+$ . It is likely that the relatively Mg-poor solutions affected the identity of the precipitated solids, as well as the extent to which they took up monovalent cations and/or excess Si. The observation that the poorly crystalline Mg-silicates precipitated in our experiments contain considerable quantities of monovalent alkali cations can be, at least in part, attributed to the kinetics of the Mg-silicate crystallization process. Brady (1992), in his study of sepiolite growth kinetics, postulated that the dehydration of  $\text{Mg}^{++}$  exerts a

limiting effect on the rate of sepiolite growth due to the relatively strong hydration of  $\text{Mg}^{++}$  in solution. Our experimental results suggest that taking some of these cations into the Mg-silicate structure is more kinetically favorable during the initial stages of Mg-silicate nucleation/growth than the construction of stoichiometric, crystalline Mg-silicates, regardless of any potential energetic costs of incorporating these cations into the proto-Mg-silicate structure.

The apparent basal d-spacing of precipitated Mg-silicates recovered from substrate-free experiments are all consistent with one another, but tend to be slightly larger and broader than would be expected for fully crystalline Mg-silicate minerals (Fig. 6). Nonetheless, as discussed above, the positions of these peaks are consistent with contributions from poorly crystalline sepiolite, whose crystalline peak is at 12.1 Å, and poorly crystalline stevensite, whose basal reflections vary between 13.6 and 15 Å in the air-dried state. Although neither the apparent d-spacings measured in our study nor the positions of FT-IR absorptions can be used to uniquely identify the presence of structural  $\text{Na}^+$  or  $\text{K}^+$ , our SEM-EDS results clearly show elevated Na content (at levels much higher than ideal stoichiometry), which indicates a relatively high proportion of  $\text{Na}^+$  and  $\text{K}^+$  cations either substituting into the crystal structure or being taken up into the interlayer (in the case of stevensite). Certainly, more research is required to understand the structural limits of  $\text{Na}^+$  and  $\text{K}^+$  incorporation into Mg-silicates during nucleation and growth.

In addition, the presence of a mineral substrate in Expts. E-H does not appear to have greatly affected the ratio or total amount of Mg and Si removal from solution (the lines corresponding to analogous substrate-free and substrate-bearing experiments in Fig. 9 plot on top of one another if drawn on the same figure). This suggests either the amount of substrate was too insignificant to affect the mineral growth regime, or that the energetics of homogeneous nucleation at these conditions are more favorable than those of heterogeneous (i.e., solid substrate) growth, or,

potentially, some combination of these two factors. Additionally, prior observations (Banfield et al., 1991) suggest that the surfaces of dioctahedral smectites not examined here may also serve as favorable nucleation surfaces for the growth of Mg-silicates.

If we normalize the number of moles of sepiolite added to Expts. E and F to be on the reference scale of moles of Mg (which can be calculated from the experiments (Table 4)), we can compare the substrate-free experiments to those initialized with sepiolite substrate. The ~0.5 mmol of Mg (in sepiolite) added to Expts. E and F is comparable to the amount of Mg precipitated in the first 6 days of Expt. I and the first 30 days of Expt. D. Thus, presumably, if all other properties (i.e., surface area, surface chemistry) of the sepiolite added to Expts. E and F were approximately the same as those of precipitated Mg-silicate (which we know to be a rough approximation on the basis of Mg/Si of the solid alone), then the initial stages of Expt. F should have behaved similarly to the second half of Expt. D and the latter ~2/3 of Expt. I. However, both Expt. F and its gibbsite-containing counterpart, Expt. H, precipitated only slightly more time-normalized quantities of Mg (2.8 and 1.6  $\mu\text{mol/day}$ , respectively) than their substrate-free counterpart, Expt. C (0.39  $\mu\text{mol/day}$ ), and did not precipitate nearly as much Mg as would be expected from the analogy with Expts. D and I. Likewise, Expts. E and G precipitated similar quantities of Mg (12 and 14  $\mu\text{mol/day}$ , respectively) as their substrate-free counterpart, Expt. A (17  $\mu\text{mol/day}$ ). Thus, the presence of a mineral substrate has little effect at these extreme supersaturations, even though the quantities of mineral substrate added to the experiments were on par with the quantities of solids formed in the early stages of the substrate-free experiments. This latter observation leads to the conclusion that the initially formed Mg-silicate nuclei are highly reactive, and also that it is energetically more favorable for the neoformed Mg-silicate to

grow upon these nuclei rather than crystalline minerals. Both of these observations are consistent with predictions from kinetic theory (e.g., Lasaga, 1998), which we discuss in more detail below.

## 5.2 Silica uptake

Together, Fig. 4, Table 2 and the low  $\Sigma\text{Cation}/\text{Si}$  ratios discussed in the previous section demonstrate that stoichiometric Mg-silicate precipitation is not the only process responsible for drawing down solution  $\text{SiO}_2$  concentrations during our experiments. This is particularly evident in experiments initialized with 0.5 mmol/kg Mg or less, whose shallow Mg vs. Si slopes suggest that silica is being taken up in considerable excess of any known Mg-silicate stoichiometry and some of which (Expts. B and C) precipitated little to no Mg-silicate. Calculations performed using our thermodynamic dataset (Sect. 3.3) as well as available experimental data (Zarubin and Nemkina, 1990) indicate that all solutions from all experiments were undersaturated with respect to amorphous silica, and, indeed, silica concentrations within a bottle containing the  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  buffer (Table 1) and 6 mmol/kg  $\text{SiO}_2$  were unchanged within the uncertainty of the measurements after 129 days (Sect. 3.1). Together, these observations confirm that neither sorption onto the LDPE bottles<sup>†</sup> (Footnote: A similar-duration test with the PC bottles used in Expts. A-C was not performed.) nor amorphous silica precipitation were plausible sinks for  $\text{SiO}_2$  during our experiments. It is thus clear that, at least in Expts. D-L, and most likely Expts. A-C, sorption onto solid phases, either incorporated as a substrate or precipitated during the experiment, is the most likely explanation for excess silica depletion. Consistent with this interpretation, sorption or excess Si uptake into Mg-silicate phases was hypothesized as an explanation for TEM observations of excess Si uptake by Mg-silicates in the alkaline Abert Lake, Oregon (Banfield et al., 1991).



Our silica uptake experiments (Table 2) yield a calculated silica uptake of  $6.4 \times 10^{-4}$  mmol/m<sup>2</sup> (0.17 mmol/g) for sepiolite and  $4.5 \times 10^{-2}$  mmol/m<sup>2</sup> (0.081 mmol/g) for talc. Although talc is not expected to have formed in our experiments, the latter experiments were run in order to enable comparison between Mg-silicates with different crystal structures and sizes. Interestingly, when normalized by mass, the Si uptake onto talc is about half that of sepiolite, whereas, when normalized by surface area, the Si uptake onto sepiolite is about 1/100<sup>th</sup> that of talc. Although the comparison is limited by our small observational set, these data suggest that, at the pH and elevated silica concentrations characteristic of alkaline lakes, the amount of silica sorbed by crystalline materials only weakly depends on that mineral's specific surface area, but depends considerably more strongly on the mineral's mass, at least over the timescales of our experiments. Our measured silica uptake onto gibbsite (0.094 mmol/g) and calcite (0.067 mmol/g) confirm this trend. The underlying mechanism controlling Si sorption onto these mineral surfaces remains unknown, however, since no single structural element is common to calcite, gibbsite, sepiolite, and talc. Together, these data help to explain the silica depletion observed in our experiments, both with and without Mg-silicate precipitation. However, if these numbers are combined with the mass of CaCO<sub>3</sub> precipitated in our experiments, they yield values considerably lower than would be required to explain the SiO<sub>2</sub> depletion in Expts. B and C, which precipitated CaCO<sub>3</sub> in the absence of significant Mg-silicate precipitation (Fig. 4). Thus, it is most likely that the spherulitic CaCO<sub>3</sub> precipitated in those experiments took up considerably more SiO<sub>2</sub> than the synthetic calcite powder we utilized in the uptake experiments.

To our knowledge, all other previously published Si sorption experiments maintain a constant mineral-to-solution mass whereas parameters such as pH and SiO<sub>2</sub> concentration were varied, making it difficult to contextualize the non-zero intercepts for our silica uptake

measurements. It is possible that these numbers indicate that our solutions were supersaturated with respect to amorphous silica by up to several tens of  $\mu\text{mol/kg}$ . Moreover, it is also possible that the surface sites on our mineral powders had simply not yet become saturated with respect to silica at the time of experimental termination (presumably, if this were the case, more time would have yielded greater silica uptake and a steeper slope which could have then yielded a zero intercept). However, regardless of whether our uptake experiments reached equilibrium, they show that the relatively low cation to silica ratio observed in our precipitated solids can be at least partially explained by the uptake of silica onto the initially precipitated Mg-silicate phase. Moreover, the fact that silica uptake can be fit with a line of constant slope suggests that the amount of silica taken up on the surface of precipitated Mg-silicates is directly proportional to the mass of the precipitate.

### 5.3 Theoretical description of Mg-silicate growth

Because our experiments were performed at similar pH and degrees of supersaturation, the results can be interpreted using the kinetic theory of mineral nucleation. This, in turn, provides considerable predictive power in understanding Mg-silicate precipitation in sedimentary environments. However, this exercise leaves us to compare what is observable in our experiments (i.e., Mg-silicate *growth*) to what is predictable from theory (i.e., Mg-silicate *nucleation*). The constant slope of the logarithm of supersaturations versus time in Fig. 5 is suggestive of exponential nucleation and growth as a function of the Gibbs free energy of reaction,  $\Delta G_r$ . For aqueous solutions, the nucleation rate ( $I$ ) may be calculated (Nielsen, 1964; Steefel and Van Cappellen, 1990; van Cappellen, 1991):

$$I = \frac{2D}{d^5} e^{-N_A \Delta G^* / RT} \quad (4)$$

where  $N_A$  is Avogadro's number ( $6.02 \times 10^{23}$  molecules/mole),  $R$  is the ideal gas constant (8314 mJ/mol·K),  $T$  is temperature (294 K for our experiments), and the aqueous species diffusion coefficient,  $D \approx 10^{-5}$  cm<sup>2</sup>/s (e.g., Oelkers and Helgeson, 1988), is used to approximate the growth rate of nuclei of diameter  $d$  at a concentration of  $1/d^3$ . Assuming, as a first-order approximation, that the nuclei are spherical, we can write:

$$\Delta G^* = \frac{16\pi v^2 \sigma^3}{3\Delta G_r^2} \quad (5)$$

where  $v$  is the molar volume,  $\sigma$  is the surface free energy of the nuclei, and

$$\Delta G_r = -RT \ln(\Omega) , \quad (6)$$

where  $\Omega$  is calculated using Eqn. 3.

Equations 4-6 allow two statements: 1) At constant temperature, the nucleation rate is very strongly dependent upon  $\Delta G_r$ , such that, below some critical value, the nucleation rates are effectively zero, and, above this value, the rates very rapidly approach infinity with increasing  $\Delta G_r$ ; and 2) Although the absolute values of  $I$  are sensitive to the values assumed for  $\sigma$ ,  $d$ , and  $v$ , the assumed value for the equilibrium constant,  $K$ , is much more critical for calculating the value of  $\Omega$  and hence  $I$ . We have chosen to utilize  $K$  of crystalline sepiolite both because the various characterization techniques we have performed suggest that our precipitated solids are mineralogically and chemically similar to sepiolite, as well as the fact that its low-temperature solubility is accurately known (Christ et al., 1973; Helgeson et al., 1978; Stoessell, 1988) and can be calculated using our thermodynamic data set. Fortunately, as discussed above, the thermodynamic solubilities of the low-temperature Mg-silicates (e.g., sepiolite, kerolite) are very similar and this decision hence has comparatively little effect on the calculations below.

If we assume that  $\sigma$  of the Mg-silicate nuclei are approximately equivalent to those of brucite, i.e.  $123 \text{ mJ/m}^2$  (van Cappellen, 1991) (Footnote: For comparison:  $\sigma_{\text{SiO}_2(\text{amorphous})} = 46 \text{ mJ/m}^2$  (van Cappellen, 1991) and  $\sigma_{\text{quartz}} = 350 \text{ mJ/m}^2$  (Parks, 1984)) and that their diameter is equivalent to the equivalent diameter of a unit cell of sepiolite (using the unit cell volume reported by Post et al. 2007):  $2 \left( \frac{3(1910.4 \text{ \AA}^3)}{4\pi} \right)^{\frac{1}{3}} \approx 15.4 \times 10^{-8} \text{ cm}$ ) and, lastly, that  $v$  is that of sepiolite ( $287.63 \text{ cm}^3/\text{mol}$  (Post et al., 2007)), we can calculate the nucleation rate as a function of  $\Omega$  (Fig. 10). Interestingly, and importantly, the value of  $\Omega$  at which the calculated values of  $I$  approach infinity very closely agrees with the critical supersaturation described by Eqn. 2. Although it would be useful to compare the reaction rates from our experiments to the calculated values of  $I$  on a quantitative basis, the experimental data cannot be meaningfully converted to nucleation rate data, since nuclei would have undoubtedly passed through the  $0.22 \text{ }\mu\text{m}$  filters used in our experiments and the data in Table 3 are hence indicative of both nucleation and growth processes.

Although these values are not strictly comparable, the close agreement between the  $\Delta G_r$  corresponding to the rapid increase in nucleation rates (20 orders of magnitude in this figure) and the rapid increase in measured Mg depletion rates, combined with the fact that the experiments initialized with a mineral seed behaved nearly identically to those without mineral seeds (Fig. 9) suggests that this  $\Delta G_r$  threshold for homogeneous nucleation is robust. Moreover, the agreement between the apparent solubility of Mg-silicate minerals calculated from Eqn. 2 suggest that the apparent solubilities of many silicates may be calculable using appropriate statements of Eqn. 4, provided that values for  $\sigma$ ,  $d$ , and appropriate thresholds for  $I$  can be attained. With this theoretical framework, the pH and temperature dependence of the apparent solubilities of these

minerals could also be estimated without the necessity of performing the many measurements required to define the apparent solubility.

## **6. Implications for presalt deposition and evolution**

In spite of their inherent complexity, the experiments and geochemical discussion we have presented in this study offer important insights into the origins of the presalt carbonates. In particular, in conjunction with previous field and experimental observations, our experiments have illustrated that the spherulitic sub-facies were likely precipitated from solutions with a pH of  $\sim 10.2 \pm 0.3$ . This pH was maintained by high concentrations of alkaline cations typical of intermediate to felsic rocks, such as  $\text{Na}^+$  and  $\text{K}^+$ , which were not counterbalanced to any significant degree by negatively charged anions such as  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . Because these anions are typical of seawater, this charge balance constraint implies minimal seawater involvement in presalt deposition. At this alkaline pH, only modest concentrations (i.e.,  $\sim 0.5$ -1 mmol/kg) of  $\text{Ca}^{++}$  were required to precipitate abundant, spheroidal  $\text{CaCO}_3$ , and the rapid rate of  $\text{CaCO}_3$  nucleation and growth at these conditions suggest it is very unlikely that  $\text{Ca}^{++}$  concentrations in the lake waters ever exceeded these modest values. These results can further be used to place quantitative constraints on  $\text{Ca}^{++}$  fluxes to the site of deposition if constraints on sedimentation rates can be derived.

Our experiments indicate that the original mineralogy of  $\text{CaCO}_3$  could have been calcite or aragonite, largely (but not exclusively) depending on the Mg/Ca ratio of the precipitating solution. The differing time scales of precipitation between  $\text{CaCO}_3$  and Mg-silicates illustrated by our experiments, however, would have tended to skew the Mg/Ca ratio towards elevated values and hence favored aragonite precipitation. Recent reports of spherulitic calcite in presalt

deposits on the Angolan margin describe relatively elevated levels of Sr (i.e., Saller et al., 2016), possibly indicative of an aragonitic component to initial mineralogy. However, Sr abundances cannot be used as unique constraints on original mineralogy unless Sr concentrations and behavior in the depositional environment are better understood.

In addition, our experiments indicate that neither elevated concentrations of organic acids, biological mediation, nor a gel matrix were required for  $\text{CaCO}_3$  to attain the spherulitic morphology. It is important to note, however, that this result cannot by itself be used to infer that biological processes were not important contributors to sedimentation and diagenesis. Microbial processes have influenced chemical and physical aspects of sedimentation in both ancient marine (Grotzinger and Knoll, 1999) and non-marine (Burne et al., 2014) carbonates. Burne et al. (2014) provide compelling evidence for microbially assisted Mg-silicate precipitation in Lake Clifton thrombolites, but it remains to be seen whether such a mechanism can operate on scales as large as the presalt depositional system. In any case, our results clearly show that elevated pH and  $\text{SiO}_2$  concentrations are the most crucial controls on the mineral-water interfacial processes which gave rise to the spherulitic morphology. This prompts the related question – how did biology contribute to the formation of presalt sediments, if at all, and in what ways might this be recorded?

Our results also permit us to conclude that only modest steady-state concentrations of  $\text{Mg}^{++}$  (i.e., 1-2 mmol/kg) would have been required to precipitate abundant, poorly crystalline Mg-silicates in the presence of elevated pH and  $\text{SiO}_2$ . Through either surface sorption or co-precipitation, these poorly crystalline Mg-silicates draw down Si from solution in excess of those which would be expected of known Mg-silicates, and additionally incorporate the pH-buffering alkaline cations  $\text{Na}^+$  and  $\text{K}^+$  into their structure. Powder X-ray diffraction data of our

experimental precipitates suggest that these initial precipitates would diagenetically crystallize to the minerals sepiolite, stevensite, or talc. Since the range of Mg concentrations which permit significant Mg-silicate growth to occur is relatively narrow, variation from this mineralogy would most likely require lower SiO<sub>2</sub> concentrations in order to achieve the higher Mg/Si ratios required to precipitate other phases such as stevensite or kerolite (Tosca and Masterson, 2014). Such fluids could potentially be generated diagenetically below the sediment-water interface, or during freshening events leading to pH decreases and SiO<sub>2</sub> precipitation.

Finally, while our experimental results provide important constraints on the influence of evaporation and high pH on the products and styles of chemical sedimentation, additional processes undoubtedly played a role in generating distinctive facies thus far identified in presalt carbonate rocks of the South Atlantic. For example, the volume and spatial extent of the presalt carbonates alone (i.e., Wright & Barnett, 2015; Saller et al., 2016) prompts fundamental questions regarding the nature of the presalt carbonate factory, its relationship to Mg-silicate generation, and the role of evaporative concentration. Also, though the co-occurrence of pore-filling Mg-silicates and CaCO<sub>3</sub> intuitively lowers reservoir quality by depleting porosity and permeability, the diagenetic processes which may affect the stability of these chemically labile minerals are not well understood. Further integration of systematic geochemical and sedimentological studies will produce holistic facies and diagenetic models that can be usefully adapted to capture the remarkable variation in these prolific deposits.

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