A rate law for sepiolite growth at ambient temperatures and its implications for early lacustrine diagenesis

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Abstract

The magnesium silicate mineral sepiolite is an important component of both alkaline lake and siliceous marine sediments. However, apart from historical constraints on its equilibrium solubility and effective solubility in surface waters, little is known about the rate at which it grows from pore waters during diagenesis. To place constraints on the early evolution of these pore waters, we have performed a series of sepiolite-seeded batch experiments at room temperature with varying concentrations of Mg and SiO₂(aq) at pH = 9.2 and 10.1. In general, the slopes of time-series measurements of Mg and Si concentrations are consistent with heterogeneous growth of a phase with sepiolite stoichiometry during the experiments within calculated uncertainties, although some slopes are more consistent with the growth of a phase with kerolite stoichiometry. In total, thirty-six individual rates were derived from the pH = 9.2 experiments and nine individual rates were determined from the pH = 10.1 experiments. In the case of the pH = 9.2 data set, fitting a simplified Transition State Theory rate law to the Si-based sepiolite precipitation rates yields:

$$\text{Rate (moles sepiolite/m}^2\text{/s)} = 10^{-16.0 \pm 0.3}(\Omega - 1)^{0.44 \pm 0.04}$$

and, for the pH = 10.1 experiments:

$$\text{Rate (moles sepiolite/m}^2\text{/s)} = 10^{-15.0 \pm 0.2}(\Omega - 1)^{0.23 \pm 0.02}$$

where Ω is the saturation index for crystalline, stoichiometric sepiolite. These results are consistent with a strong dependence of growth kinetics on pH and saturation state. The saturation state dependence is significantly stronger at pH = 9.2 than it is at pH = 10.1, such that, at extreme supersaturations approaching the critical supersaturation for homogeneous sepiolite nucleation, the calculated pH = 9.2 rates are faster than the pH = 10.1 rates. Inferences based on the uncertainties on the calculated rate parameters and the predictive capacity of the rate law suggest that these parameters can also predict the growth rates of kerolite without introducing significant additional uncertainty. Using these experimental constraints, we present a conceptual model for the evolution of pore waters during the early stages of diagenesis in sepiolite-bearing sediments. This conceptual model, which implies that exceptional sepiolite supersaturations observed in alkaline lake waters rapidly diminish as porewaters are separated during sediment burial, is in agreement with field measurements of pore waters obtained from Mg-silicate-bearing sediments.

1. Introduction

Sepiolite and similarly-comprised, Al-poor Mg-silicate minerals are unique amongst the phyllosilicates in that they readily precipitate directly from supersaturated waters at ambient temperatures and pressures (Garrels and Mackenzie, 1967; Wollast et al., 1968; Darragi and Tardy, 1987; Brady, 1992; Birsoy, 2002; Tosca et al., 2011; Tosca and Masterson, 2014; Deocampo, 2015; Tosca, 2015; Baldermann et al., 2018; Mulders et al., 2018; Tutolo and Tosca, 2018). As such, these Mg-silicates are relatively common minerals in sedimentary environments ranging from alkaline lakes to siliceous marine sediments (Kent and Kastner, 1985; Tosca, 2015). Indeed, because of their geologic prevalence, studies into their behaviour find applications across a broad swath of the Earth sciences. For example, the recent discovery and

exploitation of Cretaceous supergiant Mg-silicate-bearing reservoirs in the south Atlantic coastal margins of Brazil (Wright and Barnett, 2015) and eastern Africa (Saller et al., 2016) have reignited efforts to develop geochemical and facies models that can help to guide resource exploration efforts at these locations (Tutolo and Tosca, 2018). Moreover, recent observations of the geologic history of authigenic Mg-silicate formation in sedimentary deposits at Olduvai Gorge has offered enticing clues into the paleoclimatic record accompanying the migration of the first *Homo* species out of Africa (Deocampo et al., 2017). Together, these examples confirm the importance of placing geochemical constraints on the formation of Mg-rich phyllosilicates at ambient temperatures.

In this study, we focus specifically on the Mg-silicate mineral sepiolite, due to its chemical simplicity and widespread occurrence in the rock record. Authigenic sepiolite formation is sensitive to the salinity, Mg/Si, and pH of the precipitating solution (Tosca and Masterson, 2014; Baldermann et al., 2018; Tutolo and Tosca, 2018). Moreover, sepiolite is common in Al-poor sedimentary environments, where low detrital inputs prevent the formation of Mg-aluminosilicates such as smectites (Wollast et al., 1968; Birsoy, 2002; Calvo and Pozo, 2015; Tosca, 2015). Sepiolite observed in the geologic record is frequently accompanied by varying abundances of carbonate minerals such as calcite, aragonite, and/or dolomite (Birsoy, 2002; Yenyol, 2012; Pozo et al., 2016), although several high-purity deposits have been discovered (Pozo and Galán, 2015).

The solubility of sepiolite at ambient conditions was determined by Stoessell (1988) in a series of experiments approaching ten years in duration, yielding a solubility product (K_{sp}) for the reaction:

Additional, elevated-temperature experimentation (reviewed by Helgeson et al., 1978), and more recent revisions to the thermodynamic properties of $\text{SiO}_2(\text{aq})$ (Rimstidt, 1997; see Tutolo and Tosca, 2018 for more information), have arrived at $K_{sp} = 10^{32.07}$ at 25°C and 1 bar, which is the value that we use here to calculate the saturation state of sepiolite in our experimental solutions. It should nevertheless be noted that considerable debate remains regarding the thermodynamic solubility of sepiolite at ambient temperatures (see discussion in Baldermann et al., 2018). The *apparent* solubility (i.e. the critical level of supersaturation required to homogeneously nucleate Mg-silicate minerals directly from solution) was determined through a series of studies by Tosca and others (Tosca et al., 2011; Tosca and Masterson, 2014; Tosca, 2015); these results have since been confirmed through experimental investigation of the Mg-silicate-carbonate system (Tutolo and Tosca, 2018). These latter authors used classical nucleation theory to provide a thermodynamic reasoning for the observed critical saturation required to precipitate sepiolite at ambient temperatures. Moreover, the results of these collected experimental studies all agree with apparent solubility of Mg-silicates derived by Darragi and Tardy (1987) from geochemical analyses of evaporation of Lake Yoa. Those authors presented an apparent solubility K_{app} for the similarly-structured Mg phyllosilicate stevensite ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) equivalent to

$$K_{app} = \frac{a_{Mg^{++}}^3 a_{SiO_2(aq)}^4 a_{H_2O}^4}{a_{H^+}^6} = 10^{34}. \quad (2)$$

Stevensite is slightly more magnesian than sepiolite (Mg:Si = 0.75, versus 0.67 for ideal sepiolite), which would suggest a slightly different dependence of its solubility on pH and $a_{Mg^{++}}$ as a function of a_{SiO_2} . However, since the apparent solubility constraints provided by Eqn. 2 suggest that solutions precipitating either mineral must be 10-11 orders of magnitude supersaturated with respect to the crystalline mineral in order to nucleate, it is unlikely that this minor difference in slope affects the functionality of the critical saturation limit. To demonstrate

this, the solubility of sepiolite and kerolite, as well as the critical supersaturation required for Mg-silicate precipitation, are plotted in Fig. 1. The critical supersaturation is elevated above the thermodynamic solubilities of both minerals by approximately the same amount.

In spite of at least a half century's research into the formation of Mg-silicates from supersaturated solutions at ambient temperatures, the interactions between these minerals and pore waters during the earliest stages of diagenesis remain poorly constrained. In particular, apart from a preliminary study presented by Brady (1992) and tentative growth rates presented by Baldermann et al. (2018), the heterogeneous growth rate of sepiolite as a function of important parameters such as pH and saturation state remains almost entirely unconstrained. To address this knowledge gap, we present a series of batch experiments in which we observed the rate of depletion of Mg^{++} and $\text{SiO}_2(\text{aq})$ in solutions interacting with a sepiolite seed. The results indicate exceedingly low growth rates at near-equilibrium conditions, but a strong dependence on both pH and saturation that accelerates growth rates at elevated sepiolite saturation states. This parameterized rate law allows us to present a conceptual model for the evolution of pore waters during the early stages of diagenesis in sepiolite-bearing sediments, which, in turn, implies that exceptional sepiolite supersaturations observed in alkaline lake waters rapidly diminish as porewaters are separated during sediment burial.

2. Methods

2.1 Starting materials

Sepiolite used in the experiments is identical to that utilized by Tutolo and Tosca (2018). As reported by those authors, the specific surface area of the sepiolite is $252 \pm 7 \text{ m}^2/\text{g}$, as measured by N_2 adsorption with the Brunauer-Emmett-Teller (BET: Brunauer et al., 1938) method. Powder X-ray diffraction analyses were acquired on the sepiolite using a Panalytical

115 Empyrean Pro powder X-ray diffractometer outfitted with a Co X-ray source at the University of
116 Oxford (Tutolo and Tosca, 2018) and compared against a sepiolite reference pattern (Brauner
117 and Preisinger, 1956). This analysis (Fig. 2c) confirms that there were no impurities in the
118 samples above the detection limit, which is typically on the order of several percent. The
119 sepiolite was also imaged using an FEI Quanta 250 Field Emission Gun-Scanning Electron
120 Microscope (FEG-SEM), which confirmed the mineral's fibrous morphology and purity (Fig.
121 2a,b). In order to determine the chemical composition of the sepiolite, it was digested using 48%
122 hydrofluoric acid and 85% phosphoric acid. The resulting solution was then diluted and analyzed
123 using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). This analysis
124 yielded a Mg to Si ratio of 0.57, and trace Al (Al to Si = 0.05:1). This Mg to Si ratio is lower
125 than the ideal ratio (0.67) but consistent with the ratio (0.56) reported by Mulders and Oelkers
126 (2020). Deviations from the ideal ratio could, in principle, be caused by the presence of trace
127 (i.e., less than the several percent detection limit of XRD) amounts of quartz (or another silica-
128 bearing mineral), but SEM images strongly suggest that the samples are entirely composed of
129 fibrous sepiolite (Fig. 2a,b), and the low concentration of Al suggests that another clay mineral,
130 even if present, could not appreciably affect the Mg to Si ratio. The presence of an impurity such
131 as quartz would not significantly contribute to uncertainties on the calculation of rates, due to the
132 much larger specific surface area and much faster reaction rates of sepiolite relative to quartz.
133 Combined with stoichiometric considerations for the quantities and types of structural O and H
134 in sepiolite (Stoessell, 1977; Stoessell, 1988), the chemical measurements yield the formula:
135 $\text{Mg}_{1.77}\text{Si}_{3.11}\text{O}_{7.5}(\text{OH})\cdot 3\text{H}_2\text{O}$. The slight difference between the number of Si atoms in this
136 formula (3.11), and that in ideal sepiolite (3) – 3.7% – is negligible relative to the overall

uncertainly on the rate measurements (see below) and hence should not appreciably impact the development or application of the derived rate law parameters.

The first set of batch experiments utilized sepiolite powder that was soaked in deionized water at 60°C for 5 months. Owing to time constraints and the depletion of the supply of this powder, the rest of the experiments utilized sepiolite powder that was soaked overnight in a 0.1 M extra pure (98.5%) sodium metaborate tetrahydrate ($\text{NaBO}_2 \cdot 4 \text{H}_2\text{O}$) buffer solution and then baked at 100°C for about 24 hours, following the methodologies of Brady (1992). The differing preparation techniques did not apparently affect the results.

2.2 Experimental setup

The batch experiment design was modeled after the series of experiments presented by Brady (1992). Accordingly, all batch experiments utilized a 0.0125 M $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ buffer solution, to which Mg and Si were added. The buffer solution was prepared in a 1 L, acid-washed Low-Density Poly Ethylene (LDPE) bottle and decanted into smaller 60-250 mL LDPE bottles for individual experiments (Table 1). The pH of the solutions in these smaller bottles was adjusted to the desired value using 1 M HCl or 1 M NaOH. For the pH9, pH9-2, pH9-3, pH10, and pH10-2 experiments, desired initial Mg concentrations were achieved by adding American Chemical Society (ACS) reagent-grade magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) directly to the solutions. For the rest of the experiments, 0.25 M MgCl_2 brine, prepared using ACS reagent-grade $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and ultrapure (18 M Ω -cm), was added to the solutions via pipette. The latter preparation method enabled swifter, more accurate Mg additions. Desired SiO_2 concentrations were achieved through addition of Baker Analyzed[®] sodium metasilicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) directly to the solutions.

In all experiments, 0.5 grams of sepiolite were added for every 125 mL of solution. An additional blank experiment was performed without a sepiolite seed to evaluate the possibility of homogeneous mineral nucleation at our experimental conditions. The solutions were mixed on an orbital shaker and kept in a climate-controlled ($22 \pm 1^\circ\text{C}$) laboratory. Throughout the experiments, 3 or 4 mL samples were taken periodically every 2-8 hours using a syringe. Rate calculations (discussed in more detail below) take explicit account of solution volume changes resulting from sampling, and these are recorded in Table 1. Immediately after sampling, solutions were preserved for analysis and analyzed for Si, Mg, and Na using methods described in Section 2.3. The pH was measured on an aliquot of each sample at specified times using a Thermo Scientific™ PerpHecT™ Orion™ ROSS™ combination pH micro-electrode, which was calibrated at least daily using NIST-traceable pH 4, 7, and 10 buffers. Some experiments were repeated in order to verify results; this was done following the same steps as previously mentioned.

Initial fluid chemistry was varied to achieve a range of sepiolite saturation states while still remaining below the critical supersaturation for homogenous nucleation of Mg-silicate minerals (Fig. 1 and associated discussion). Decisions for initial solution Mg to Si ratios were informed by previous experimental studies (Tosca and Masterson, 2014; Tutolo and Tosca, 2018) examining the control that Mg/Si ratio plays on Mg-silicate precipitation at ambient temperatures. Most relevant to the present study, Tosca and Masterson showed that, at pH = 9, a sepiolite-like phase (ideal Mg/Si = 0.67) generally only precipitates from solutions with $\text{Mg/Si} \leq 1$, while the more silica-rich stevensite and kerolite phases tend to precipitate at $\text{Mg/Si} > 1$ in this system. In their higher pH (=9.4) experiments, kerolite and/or stevensite (both have an ideal Mg/Si = 0.75) dominated their reaction products regardless of the Mg/Si of the precipitating

solution (0.67 – 6). Tutolo and Tosca (2018) followed on this study by performing experiments at pH = 10.1 and Mg/Si ranging from 0.0167 to 0.33, effectively filling out the lower range of the Mg/Si compositional space that had not been explored by Tosca and Masterson (2014), which those authors hypothesized to be more representative of evaporation-dominated, SiO₂-rich alkaline lakes. Tutolo and Tosca (2018) used chemical and x-ray diffraction measurements of solid run products and measured depletions of Mg⁺⁺ and SiO₂ from their experimental solutions to infer that their experiments produced sepiolite with a loughlinite (i.e., the Na analogue of sepiolite) and/or stevensite component. Although the cation (0.5(Na + K) + Mg) to Si ratios of their precipitates (0.43 ± 0.10 to 0.59 ± 0.19) values were generally still too low to indicate stoichiometric sepiolite (Mg:Si = 0.67), they are consistent with the Mg to Si ratio of the sepiolite used in this study (0.57). Together, this series of studies suggests solutions with Mg/Si ≲ 1 are ideal for sepiolite precipitation from ambient-temperature solutions. Accordingly, the initial Mg/Si for our experiments ranged from ~0.1 – 1.1.

2.3 Solution analyses

Solutions for cation analysis were filtered using 0.22 µm Nylon syringe filters, acidified and diluted, and then stored in tightly sealed 15 mL centrifuge tubes and refrigerated while awaiting analysis. Cations (Mg, Na, and Si) were analyzed using a Varian 725-ES Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The ICP-OES was calibrated ($r^2 > 0.999$) via serial dilution of certified standards (BDH Limited). Analytical precision and accuracy for these analyses is typically better than ±5%; this value (5%) is used to calculate the error on growth rates below. As noted in the discussion of the rate calculations, this assumed error may be overly conservative in some instances.

2.4 Reaction Stoichiometry and Rate Calculations

Measured Si and Mg concentration data were screened to remove spurious and duplicative data points prior to rate calculations. All measured data from all experiments was fit using a York regression strategy that takes account of errors on both x- and y-variables (York et al., 2004), as implemented by Wiens (2020). In numerous cases (Expts. pH9-3, pH9-3rep, pH10-2, pH10-3, pH10-5), the slope of the line fit to Si and Mg concentrations was significantly different when the first measured concentrations were included in the fit than if they were excluded. Visual inspection of these measurements clearly demonstrated that they were out of trend with respect to the subsequent analyses, and these measurements were therefore removed from consideration in the rate calculations below. It is possible that these initial points were affected by an initial period of Mg and Si depletion through sorption (as observed in titration experiments by Brady (1992)) or anomalously high reactivity that was subsequently minimized. Typically, sorption processes are kinetically fast (Stumm and Morgan, 1996), and of limited extent in the sepiolite system (Brady, 1992; Tutolo and Tosca, 2018), and thus would likely only affect this early-time data. Moreover, anomalously high reactivity, if it was occurring, did not apparently affect subsequent measurements which adhered to a consistent slope. In addition to these out-of-trend initial points, several samples obtained during the experiments were, for all intents and purposes, duplications of each other. Due to laboratory schedules and a general uncertainty about the expected rates of Si and Mg depletion during the first set of experiments (Expts. pH9 and pH10), multiple samples were obtained over a short period of time, and these samples all yielded measured Mg and Si concentrations within error of one another. In these cases, the mean of the measurements (including the time at which they were obtained) was used in the calculation of precipitation rate. Finally, in several experiments (Expts. pH9, pH10, and pH10-5), the final measured concentration was not significantly different than the penultimate

measurement. In these cases, the rate had likely slowed so significantly that no further depletion was occurring over the timescale of the measurement, and, thus, these data points were not used in the calculations. Table 1 includes all data used in the calculation of rates; the measurements that are the mean of multiple back-to-back measurements are also denoted.

Due to the design of the experiments, it is unfortunately difficult, if not impossible, to verify the crystallinity and chemical formulas of the precipitates formed during our experiments, other than through the inference techniques described in the previous paragraph. Specifically, in order to preserve the ability to accurately normalize the observed growth rates by the mineral surface area in an experiment, a key requirement is ensuring that only very limited amounts of growth (on a mass-normalized basis) occur over the duration of an experiment. This is because, at high net amounts of growth, the surface area of the mineral in the experiment will change, possibly dramatically, in difficult to discern ways, and thereby bias the growth rate calculation. However, because this experimental design requires negligibly small amounts of growth, one cannot reasonably expect to quantify the mineralogy or chemistry of the precipitated phase via any traditional characterization techniques. For example, x-ray diffraction, with a detection limit on the order of several percent, would be unable to discern the amounts of growth that occurred in our experiments (up to ~5%): assuming it is possible that *all* of the material precipitated during the experiments was *not* sepiolite, this would be just barely at the detection limit for the XRD measurements, under ideal conditions for identifying crystallographically distinct phases. However, given the coupled Mg and Si depletion during all experiments, it is likely that the material that precipitated had a structure akin to sepiolite or, if it was not sepiolite, another similarly-structured Mg-silicate phase, making identification by XRD unrealistic. The significant interaction volumes inherent in chemical identification techniques such as Scanning

Electron Microscopy – Energy Dispersive Spectroscopy and Electron Microprobe similarly prevent chemical identification of such a small amount of overgrowth on material with virtually identical chemical composition. For these reasons, we are forced to rely on solution chemistry, and post-experiment SEM imagery, to infer the chemical identity of the material that precipitated during our experiments.

The rate of sepiolite growth (R , mol/m²/s) was calculated according to:

$$R = \frac{V \Delta C}{\nu S \Delta t} \quad (3)$$

where V is the volume of the solution during the time interval (Δt) between the previous sample and the current sample, ΔC is the measured change in concentration of the applicable element (either Si or Mg), ν is the stoichiometric number of the element in the sepiolite structure, and S is the surface area of sepiolite in the reactor (i.e., the BET specific surface area multiplied by the mass of mineral added to the experiment).

As discussed above, previous studies have illustrated that sepiolite may precipitate with a loughlinite (i.e., the Na analogue of sepiolite) component in Na-bearing solutions at ambient temperatures (Tutolo and Tosca, 2018). The precipitation of a Na component in the neoformed precipitate and the potential for an accompanying Na⁺-for-Mg⁺⁺ exchange reaction as it crystallizes, could potentially contribute to inaccurate results if the changes in Mg⁺⁺ concentration are used to derive rates. Unfortunately, the uncertainty on the Na concentrations (Table 1) do not permit an accurate determination of the amount of Na entering into or departing out of the neoformed precipitate over the course of the experiments. Thus, we use Si in the derivation of rate parameters below, although the Mg-derived rates are still calculated and reported. Importantly, interaction of even chemically pure loughlinite with Mg-bearing solutions has the effect of converting loughlinite to sepiolite (Fahey et al., 1960), and

precipitation rates of sepiolite with a minor loughlinite component would nevertheless require a stoichiometric cation-to-Si ratio to maintain charge balance. Thus, the Si-based rates are expected to be representative of the growth a phase with sepiolite stoichiometry, regardless of any other cations incorporated and non-stoichiometric ratios observed in the experiments.

2.5 Geochemical Calculations

Saturation state (Ω) with respect to sepiolite, $a_{SiO_2(aq)}$, and $a_{Mg^{++}}/a_{H^+}^2$ for each sample were calculated using the Geochemists Workbench v. 12.0.5 (Bethke et al., 2018), outfitted with the thermodynamic database presented by Tutolo and Tosca (2018). Specifically, saturation state was calculated according to:

$$\Omega = \frac{Q}{K} \quad (4)$$

where Q is the calculated ion activity product for the stoichiometric sepiolite dissolution reaction (Eqn. 1), and K is the equilibrium constant for sepiolite dissolution (i.e., the line labeled “sepiolite solubility” in Fig. 1; see Tutolo and Tosca (2018) and Sect. 1 above for details). Calculations utilized the extended Debye-Hückel “B-dot” expression for the calculation of activity coefficients of charged species (Helgeson, 1969), and assume a value of unity for the activity coefficients of neutral species. We assume that the effect of using the “ideal” sepiolite stoichiometry (Eqn. 1) versus that specifically applicable to the sepiolite used in our experiments has a limited effect on our calculated values of Ω , and that this effect can wholly be accounted for by the assumed uncertainty on values of $(\Omega-1)$ in rate law determinations below. Apart from the measured Mg, Na, and Si concentrations and pH, these calculations required estimates for $B(OH)_3(aq)$ and Cl^- concentrations, which were not measured in our analyses. Thus, we assumed that $B(OH)_3(aq)$ concentrations were 0.0125 mol/L, consistent with the amount of

sodium metaborate added. As a starting guess, a concentration of Cl^- equivalent to $2\times$ the initial Mg was added; this Cl^- was then adjusted by the code to achieve charge balance.

2.6 Rate law parameterization

Past work in the Mg-silicate system has demonstrated that Mg-silicate precipitation is strongly dependent upon solution saturation state (Darragi and Tardy, 1987; Brady, 1992; Tosca et al., 2011; Tosca, 2015; Tutolo and Tosca, 2018), and it is thus important to accommodate this dependence when deriving a rate law from our experimentally determined Mg-silicate precipitation rates. Typically, this saturation state dependence is accounted for through the following, generic Transition State Theory-based rate law (Aagaard and Helgeson, 1982; Lasaga, 2014):

$$\text{Rate} = k(\Omega - 1)^n \quad (5)$$

where k is the rate constant in $\text{mol/m}^2/\text{s}$ and n parameterizes the dependence of the overall rate on the saturation state. Values of n likely encapsulate further information regarding the mechanism of growth during the experiments (Schott et al., 2012), but detailed investigation of processes at this scale in the context of the present study is difficult given the dearth of phyllosilicate growth data from the literature to compare against. Brady (1992) advocated for the use of a version of this rate law that incorporated an additional, stoichiometric dependence of the rate on Ω (i.e., a value of the Temkin number (Lichtner, 2016)). However, we favor the use of Eqn. 5 due to the apparently significant variability of the stoichiometry of natural and experimentally formed sepiolite specimens as well as the assertion that adding more complexity to this simple relationship is unwarranted on the basis of the current state of our knowledge of phyllosilicate growth rates at ambient temperatures. When fitting Eqn. 5 to the experimentally determined rate data, uncertainty on individual rates was calculated according to error

propagation techniques presented by Rimstidt (2014) by including the uncertainty on both ΔC and S in Eqn. 3. A universal uncertainty of ± 0.5 log units was used to account for uncertainties on calculated values of $(\Omega-1)$. This latter value is a conservative estimate intended to account for potential uncertainties related to the stoichiometry and crystallinity of both the initial sepiolite and neoformed precipitate as well as errors on calculated aqueous species activities and thermodynamic properties.

3. Results

3.1 Reaction stoichiometry and growth regime

Experimental results are consistent with the heterogeneous growth of a phase with sepiolite ($Mg/Si = 0.67$ (ideal) or 0.57 (starting material)) or potentially kerolite ($Mg/Si = 0.75$) stoichiometry from experimental solutions (Figs. 3,4, Table 1). The stoichiometry of Mg and Si depletion ranged from 0.56 ± 0.18 to 0.90 ± 0.22 in the $pH = 9.2$ experiments and from 0.47 ± 0.14 to 0.81 ± 0.05 in the $pH = 10.1$ experiments (Fig. 3, Table 1). The greatest uncertainty on the calculated slopes generally coincide with experiments that have the fewest measurements, although these lines generally reproduce the measured values just as well as other lines with smaller uncertainties on their slopes. In general, the slopes of these lines were greater than the Mg/Si ratio of the sepiolite used in the experiments (0.57), but many agreed with this value within calculated uncertainties. Moreover, slopes calculated from repeated experiments (i.e., pH9, pH9rep, and pH9rep2; pH 9-3 and pH9-3rep) are in good agreement with one another, and these experiments show similar overall trends (Fig. 4). Values of $a_{SiO_2(aq)}$ and $a_{Mg^{++}}/a_{H^+}^2$ calculated from the experimental measurements demonstrate that all but two of the measurements were below the critical supersaturation for Mg-silicate growth at ambient temperatures, and that all but these same two points were undersaturated with respect to brucite

(Fig. 4). Although the final samples from several experiments indicated that no measurable depletion was occurring over the timescale of the measurement, all experimental measurements remained significantly supersaturated with respect to sepiolite (and kerolite) at their termination (Fig. 4). The physical characteristics of the sepiolite material used in the experiments did not discernably change over the course of the experiments (Fig. 5)

3.2 Rate determinations and associated uncertainties

In total, thirty-six individual rates were derived from the pH = 9.2 experiments and nine individual rates were determined from the pH = 10.1 experiments (Table 1). Sepiolite precipitation rates calculated from the changes in solution chemistry during these experiments range from 1.1×10^{-11} to 1.3×10^{-14} mol/m²/s in the pH = 9.2 experiments and from 1.5×10^{-12} to 1.1×10^{-14} mol/m²/s in the pH = 10.1 experiments, with rates decreasing in both experiments with decreasing values of Ω (Table 1, Fig. 6). Errors on individual rate determinations from the pH = 9.2 experiments tend to be greater, in general, than those calculated for the pH = 10.1 experiments. The precipitation rate recorded in the pH = 9.2 experiments was generally slower, yielding generally lower values of ΔSi or ΔMg (depending, of course, on the Δt between any two individual measurements). For three of the pH = 9.2 experiments, these factors compounded together to yield calculated errors on the ΔSi or ΔMg measurements that were greater than the magnitude of the ΔSi or ΔMg concentration measurements themselves (these are the largest error bars in Fig. 6a). Even in these cases, however, the calculated rates adhere to the trends created by rate determinations with lower proportional errors, suggesting that the assumed error on concentration measurements may be overly conservative in some instances.

3.4 Rate law for sepiolite growth

The collected values of rates, saturation states, and their associated uncertainties permits fitting of the simplified Transition State Theory rate law (Eqn. 5) to the pH = 9.2 and pH = 10.1 data sets. In the case of the pH = 9.2 data set, this fitting process (Sect. 2.6) yields the rate law:

$$\text{Rate (mol/m}^2\text{/s)} = 10^{-16.0 \pm 0.3} (\Omega - 1)^{0.44 \pm 0.04} \quad (6)$$

and, for the pH = 10.1 experiments:

$$\text{Rate (mol/m}^2\text{/s)} = 10^{-15.0 \pm 0.2} (\Omega - 1)^{0.23 \pm 0.02} \quad (7)$$

Equations 6 and 7 yield values of $R^2 = 0.53$ and 0.68 , respectively, when comparing logarithms of predicted rates versus measured values, consistent with the generally greater scatter in the pH 9.2 rate data relative to that from the pH 10.1 experiments. The rate constant ($10^{-16 \pm 0.3}$ mol/m²/s) extracted from the pH = 9.2 experiments is an order of magnitude lower than that extracted from the pH = 10.1 experiments ($10^{-15.0 \pm 0.02}$ mol/m²/s), consistent with the generally faster precipitation rates observed in the latter experiments. Moreover, the dependence of log(Rate) on log($\Omega - 1$) is about twice as strong at pH = 9.2 ($n = 0.44 \pm 0.04$) than at pH = 10.1 ($n = 0.23 \pm 0.02$), consistent with the steeper increase in precipitation rates as a function of ($\Omega - 1$) observed in the pH = 9.2 experiments (Fig. 6).

In general, concentrations of Si and Mg calculated using the derived rate parameters are in good agreement with those measured during the experiments (Fig. 7). Although changes in Si and Mg (ΔSi and ΔMg , respectively) calculated from the derived rate equations have a tendency to under-predict measured changes (Fig. 8), the calculated and measured changes in Si concentrations generally agree or very nearly agree within the error of the measurements, and all but a handful of calculated changes are within an order of magnitude of the measured changes. The calculated values of ΔSi are generally in better agreement with measured values of ΔSi than the calculated and measured values of ΔMg , however (Fig. 8). This observation is consistent

with the use of the former (ΔSi) to ultimately derive the growth rate parameters (Fig. 6, Eqns. 6,7; see discussion in Section 2.4).

4. Discussion

4.1 Evaluation of the derived rate parameters for sepiolite growth

The precipitation of phyllosilicate minerals is an exceedingly common process in Earth's near-surface environments, and authigenic Mg-silicate minerals like sepiolite present a particularly widespread and promising group of minerals for interpreting past Earth surface conditions. However, the lack of parameterized rate equations for the growth of these minerals remains one of the biggest challenges preventing the quantitative application of geochemical models to the interpretation of these processes. In this study, we have derived the first fully parameterized and vetted rate law for calculating sepiolite growth rates at ambient temperature. In turn, the experimental techniques employed here can be expanded to aid our understanding of the growth rates of many other phyllosilicates at Earth's surface conditions.

Although, due to the lack of data in the literature, it is difficult to compare our determined growth rates with previous rate determinations, several data sets can yield interesting context for our results. For example, it is intriguing to note that our measured rates, which span 3 orders of magnitude from 10^{-11} to 10^{-14} mol/m²/s (Fig. 6), overlap the sepiolite dissolution rates determined by Mulders et al. (2020) at pH = 9.2 and 9.7 ($\sim 10^{-13}$ mol/m²/s), although it should also be noted that the substantial saturation state dependence causes our rates drop to $\sim 10^{-16}$ mol/m²/s and $\sim 10^{-15}$ mol/m²/s as equilibrium is approached (Fig. 9a), and the dependence of sepiolite dissolution rates on the approach to equilibrium is not constrained. Our rates also compare favorably with the sepiolite precipitation rates inferred by Baldermann et al. (2018) – their results (which were not surface area-normalized) yield values on the order of 10^{-10} - 10^{-12}

mol/m²/s when assuming that the specific surface area of the several micrograms of sepiolite nucleated during their experiments was similar to that of the sepiolite used in our experiments. Additionally, the increasing rates with increasing pH observed in our experiments is also consistent with similar observations presented by both Brady (1992) and Baldermann (2018). Finally, our rates are slightly slower than the high-pH brucite precipitation rates reported by Pokrovsky and Schott (2004) ($\sim 10^{-9} - 10^{-10}$ mol/m²/s), which is consistent with the hypothesis that Si tetrahedra addition to Mg octahedral sheets is the rate-limiting step during Mg-silicate growth (Tutolo et al., 2018).

4.2 Precipitate stoichiometry and rate law applicability to other Mg-silicate minerals

Due to the challenges described in Section 2.4 above, it is exceedingly difficult to directly and unambiguously determine the crystallinity and chemical composition of the solid material precipitated in our experiments. Although the stoichiometry of Mg and Si depletion in our experiments are consistent with the stoichiometry of sepiolite, there is significant scatter in the slopes, and several experiments yielded precipitates with an apparent stoichiometry that is somewhat higher than sepiolite, even when errors in the slopes are taken into account. It is therefore worth considering the consequences of differing precipitate stoichiometries on the predictive capacity of our rate parameters.

Out of simplicity, and to remain consistent across all experiments, our rate parameters were derived by assuming that our experiments precipitated a mineral that was chemically identical to our starting material—i.e., the rates are calculated by dividing the sepiolite surface area-normalized rates of Si depletion by the number of Si atoms in the structure of the sepiolite material used in our experiments (3.11). If, rather than sepiolite, a phase with kerolite stoichiometry was precipitating during the experiments, a possibility that is indeed consistent

with the experiments that had the highest Mg/Si slopes, then the number of Si atoms by which we would have needed to normalize would be 4 (Stoessel, 1988). Assuming that a phase with kerolite stoichiometry grows at approximately the same rate on sepiolite as it does on kerolite (which is true of gibbsite growth on kaolinite and muscovite (Nagy et al., 1999)), using 4 instead of 3.11 for the number of Si atoms per formula unit would ultimately yield rates that were 29% higher than they should be. Importantly, this 29% error would be within the errors on the derived rate constants (Equations 6 and 7), and well within the approximately order of magnitude-level predictivity of the presented rate law (Fig 7). Thus, considering: 1) this context for the stoichiometry of the precipitates; 2) the relative similarity of the equilibrium solubilities of kerolite and sepiolite (Fig. 1); and 3) the assumed ± 0.5 log unit error on the values of $(\Omega-1)$ in the derivation of the rate parameters (Sect. 2.6) suggests that, without additional, more precise knowledge of the growth rates of either phase, the growth rates of both kerolite and sepiolite can actually be modeled with the rate parameters that we present without introducing additional uncertainty into the predictions.

4.3 Implications for early diagenesis in alkaline lakes

A conceptual model for the evolution of sepiolite saturation state during early diagenesis in sepiolite-forming alkaline lakes is presented in Fig. 9. Previous work in this system (reviewed in Sect. 1 above) has demonstrated that Mg and Si concentrations in alkaline lake waters are controlled by the critical supersaturation required for the homogeneous growth of Mg-silicates (Fig. 1). Provided that silicifying organisms are not significantly depleting Si concentrations, this thermodynamic control on sepiolite nucleation will enforce a strong and constant supersaturation of lake waters with respect to sepiolite and contribute a flux of sepiolite surface area to the lake floor sediments as lake waters evolve during evaporative concentration (e.g.,

Darragi and Tardy, 1987; Tosca, 2015; Tutolo and Tosca, 2018). Upon pore water occlusion from the overlying water column in these systems, however, the pore waters will no longer be limited by homogeneous nucleation constraints, but rather by the heterogeneous growth of sepiolite, which is rapid at saturation states near the Mg-silicate critical supersaturation, but slows dramatically as pore fluids approach equilibrium with respect to sepiolite (Fig. 9a). This kinetic behaviour will produce a profile of sepiolite saturation state as a function of burial depth that will vary as a function of the pore water pH, burial rate, and availability of Mg and Si (Fig. 9b). Interestingly, the rate of sepiolite growth calculated from our derived rate equations implies that, at levels of supersaturation approaching the critical supersaturation for Mg-silicate minerals (i.e., those representative of the pore waters right at the sediment-water interface), the rate of sepiolite precipitation at pH = 9.2 is faster than that at pH = 10.1 (Fig. 9a). This suggests that, given similar fluxes of sepiolite surface area, these lower-pH pore waters will more rapidly approach sepiolite equilibrium during the earliest stages of pore water diagenesis. Nevertheless, over longer time scales and during deeper burial, our rate expressions suggest that the higher pH pore waters will be more readily able to approach sepiolite equilibrium.

The observation of massive, relatively pure sepiolite successions in the geologic record (Pozo and Galan, 2015) and demonstrated reductions in Mg-silicate saturation state in lacustrine pore waters (e.g., Stoessell and Hay (1978), reviewed by Tosca (2015)) suggests a role for the growth of sepiolite during early diagenesis in these systems. However, until now, it has been impossible to disentangle the relative roles of water column precipitation and diagenetic growth of sepiolite versus silica and Mg-bearing carbonates (e.g., dolomite, (hydro-)magnesite) during sedimentation and early diagenesis. Our derived rate parameters permit, for the first time, quantification of the evolution of Mg-silicate growth during sediment burial, which, when

combined with literature data for the behavior of silica and Mg-bearing carbonates (e.g., Kent and Kastner, 1985; Power et al., 2019), can aid the development of fully coupled models for these systems. At the most basic level, the dramatic increase in the growth rate with increasing saturation state and pH helps to explain the observation that many natural waters, including seawater, are persistently and metastably supersaturated with respect to sepiolite while pore waters in their underlying sediments tend to approach equilibrium with this mineral. Ultimately, however, the factors that control sepiolite growth in alkaline lakes or their underlying sediments are a complex function of the chemistry (i.e., alkalinity, pH, and Mg and Si concentrations) of the lake and pore waters, degrees and rates of evaporation in the lake waters, and the availability of sepiolite growth surfaces in the sediments, and thus require the implementation of fully coupled models to disentangle individual processes (e.g., Milesi et al., 2020).

Due to the simplicity of the rate equations that we have employed, the parameters that we present here for calculating sepiolite growth rate can be directly used in any geochemical modeling software capable of modeling mineral dissolution and growth kinetics using standard Transition State Theory rate laws. Thus, these rate parameters can help to guide the development of facies models for hydrocarbon exploration in sepiolite-bearing systems as well as attempts to use sepiolite-rich sedimentary rocks to decipher past environmental conditions. Evaluating future and previously published field studies in the context of the rate law we present here should thus provide useful insight into the processes that control the formation and evolution of Mg-silicates at Earth surface conditions.

5. CONCLUSIONS

The magnesium silicate mineral sepiolite is an important component of both alkaline lake and siliceous marine sediments, but little is known about the rate at which it grows from pore

waters during diagenesis. To address this significant knowledge gap, we have performed a series of sepiolite ($\text{Mg}_{1.77}\text{Si}_{3.11}\text{O}_{7.5}(\text{OH})\cdot 3\text{H}_2\text{O}$)-seeded batch experiments at room temperature with varying concentrations of Mg and $\text{SiO}_2(\text{aq})$ at pH = 9.2 and 10.1. In total, thirty-six individual rates were derived from the pH = 9.1 experiments and nine individual rates were determined from the pH = 10.2 experiments. These results are consistent with a strong dependence of sepiolite growth kinetics on pH and sepiolite saturation state. The saturation state dependence is around twice as strong at pH = 9.2 than it is at pH = 10.1. Inferences based on the uncertainties on the calculated rate parameters and the predictive capacity of the rate law suggest that the derived rate law can also predict the growth rates of kerolite without introducing significant additional uncertainty. Using these experimental constraints, we present a conceptual model for the evolution of pore waters during the early stages of diagenesis in sepiolite-bearing sediments. This conceptual model, which implies that exceptional sepiolite supersaturations observed in alkaline lake waters rapidly diminish as porewaters are separated during sediment burial, is in general agreement with field measurements of pore waters obtained from Mg-silicate-bearing sediments, although future modelling work and field studies are required to disentangle these complex processes.

Declaration of Competing Interest

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

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Figure Captions

Figure 1 Activity-activity plot illustrating the solubility of sepiolite and the critical supersaturation required for the homogeneous nucleation of Mg-silicate minerals at ambient temperatures and pressures. The equilibrium solubility of kerolite (Stoessell, 1988) is also plotted for comparison (see text).

Figure 2 Scanning electron microscopy (SEM) images of sepiolite used in batch experiments (a, b) and X-Ray Diffraction pattern of sepiolite used in batch experiments, with the reference pattern for sepiolite (Brauner et al. 1956) shown in blue.

Figure 3 Mg and Si concentrations measured during sepiolite precipitation experiments. Fitted slopes of the lines, and accompanying (1σ) uncertainties are denoted for each experiment.

Figure 4 Activity-activity diagram demonstrating that all but two of our experimental measurements were below the critical supersaturation required for the heterogeneous nucleation of Mg-silicate minerals (see Tutolo and Tosca, 2018) and the thermodynamic solubility of brucite. These two measurements were not apparently affected by the precipitation of either mineral (Fig. 3).

Figure 5 A representative post- experiment image of the sepiolite, demonstrating that no significant physical changes had occurred.

Figure 6 Logarithm of sepiolite precipitation rate plotted as a function of the solution supersaturation state (represented as $\log(\Omega - 1)$) at pH =9.2 (a) and 10.1 (b). The rate laws (lines) were fit to the plotted data (circles), taking into account the uncertainty on both the plotted rates and calculated values of $\log(\Omega - 1)$.

Figure 7 Cross-plots of calculated and measured Si and Mg concentrations. Calculations were performed using the rate laws presented in Fig. 3.

Figure 8 Logarithms of the ratios of calculated and measured changes in Si and Mg concentrations (ΔSi and ΔMg , respectively) as a function of Si and Mg concentration at the beginning of the time interval over which the change occurred. Calculations were performed using the rate laws presented in Fig. 3. Error bars assume that the uncertainty on the difference calculation is equivalent to the uncertainty on the calculated value of ΔSi or ΔMg . Dashed lines represent one order of magnitude in either direction of unity.

Figure 9 a. Integration of heterogeneous rate laws derived in this study with previous knowledge of the Mg-silicate growth regime in alkaline lake systems. Critical Mg-silicate supersaturation is consistent with Figs. 1 and 3, and the Mg-silicate nucleation rate was calculated using equations and parameters given by Tutolo and Tosca (2018). b. Conceptual model of sepiolite saturation state evolution during sedimentation and early diagenesis in alkaline lakes. Water column saturation state is controlled by the critical supersaturation for the homogeneous nucleation of Mg-silicate minerals, while pore waters approach equilibrium with respect to sepiolite as sediments are buried. The derived rate laws demonstrate that shape of these saturation profiles will depend on both pH of the pore fluids and the rate of sediment burial.

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Table

Table 2 Chemical and rate information for all presented experiments														
Time	Na	Si	σSi	Mg	σMg	pH	Ωsepiolite	Volume	log(<i>a</i> SiO ₂ (aq))	log(<i>a</i> Mg/ <i>a</i> ² H ⁺)	log (<i>R</i> _{Si})	log(σ <i>R</i> _{Si})	log (<i>R</i> _{Mg})	log(σ <i>R</i> _{Mg})
(s)	(mmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)			(mL)			(mol/m ² /s)		(mol/m ² /s)	
pH9	252 ± 7 m ² sepiolite; m = 0.87 ± 0.07													
0	14.6	709	35	796	40	9.23	8.99	250	-3.26	15.15				
8940	14.6	658	33	737	37	9.27	8.93	246	-3.30	15.20	-11.74	0.41	-11.43	0.40
17400	14.6	639	32	718	36	9.22	8.47	242	-3.30	15.09	-12.15	1.05	-11.91	1.18
80340*	14.6	506	25	601	30	9.20	7.42	236	-3.40	14.97	-12.18	0.13	-12.00	0.17
167520*	14.3	466	23	556	28	9.20	7.08	228	-3.43	14.94	-12.86	0.37	-12.57	0.40
433195*	14.8	371	19	472	24	9.17	6.00	218	-3.53	14.81	-12.99	0.14	-12.79	0.19
504982	15.2	355	18	460	23	9.21	6.10	210	-3.55	14.88	-13.21	0.70	-13.09	1.19
1628182	13.8	219	11	360	18	9.19	4.32	206	-3.76	14.74	-13.49	0.07	-13.38	0.13
pH9rep	61 ± 2 m ² sepiolite; m = 0.70 ± 0.15													
480	14.9	867	43	707	35	9.23	9.30	57	-3.17	15.10				
87600	14.3	699	35	595	30	9.19	8.19	54	-3.26	14.95	-12.23	0.14	-12.17	0.18
174600	14.1	630	32	538	27	9.18	7.68	51	-3.30	14.89	-12.64	0.30	-12.48	0.31
437220	14.3	549	27	487	24	9.16	7.01	48	-3.36	14.80	-13.08	0.22	-13.03	0.31
522360	14.3	529	26	470	24	9.19	7.06	45	-3.38	14.85	-13.22	0.83	-13.05	0.86
pH9rep2	61 ± 2 m ² sepiolite; m = 0.83 ± 0.13													
1920	14.8	762	38	708	35	9.27	9.24	57	-3.24	15.18				
74820	15.3	618	31	516	26	9.26	8.08	54	-3.32	15.02	-12.22	0.15	-11.85	0.10
77733	14.8	505	25	465	23	9.24	7.25	51	-3.41	14.94	-10.95	0.15	-11.05	0.30
340533	15.5	437	22	421	21	9.26	6.82	48	-3.47	14.94	-13.15	0.21	-13.10	0.31
425733	15.1	411	21	386	19	9.22	6.25	45	-3.49	14.82	-13.11	0.50	-12.74	0.35
pH9-2	126 ± 4 m ² sepiolite; m = 0.74 ± 0.06													
11880	17.6	943	47	803	40	9.24	9.75	121	-3.14	15.16				
88980	17.6	731	37	609	30	9.32	9.15	117	-3.27	15.20	-12.07	0.12	-11.87	0.11
337440	18.3	622	31	521	26	9.31	8.38	113	-3.33	15.12	-12.88	0.19	-12.73	0.20
511260	18.4	566	28	485	24	9.25	7.62	109	-3.36	14.96	-13.03	0.33	-12.98	0.43
685620	16.3	459	23	416	21	9.33	7.37	105	-3.47	15.07	-12.77	0.15	-12.71	0.20
2258520	16.1	281	14	285	14	9.26	4.99	101	-3.67	14.77	-13.52	0.07	-13.41	0.08
pH9-3	126 ± 4 m ² sepiolite; m = 0.65 ± 0.14													
85560	15.8	694	35	130	7	9.34	6.52	117	-3.29	14.59				
170460	15.6	682	34	124	6	9.32	6.27	113	-3.30	14.53	-13.38	1.76	-13.43	0.65
423780	15.6	626	31	93	5	9.28	5.29	109	-3.32	14.32	-13.20	0.36	-13.21	0.11
608580	16.2	582	29	47	2	9.10	2.67	105	-3.32	13.67	-13.18	0.42	-12.92	0.05
1829340	15.4	521	26	25	1	9.25	2.34	101	-3.40	13.70	-13.87	0.28	-14.07	0.05
pH9-3rep	61 ± 2 m ² sepiolite; m = 0.56 ± 0.18													
86280	16.1	722	36	155	8	9.22	6.13	54	-3.25	14.42				
172980	15.5	655	33	122	6	9.21	5.41	51	-3.29	14.30	-12.65	0.32	-12.72	0.13
435780	15.5	600	30	87	4	9.22	4.66	48	-3.33	14.18	-13.25	0.35	-13.20	0.09
520980	15.7	583	29	79	4	9.22	4.42	45	-3.34	14.13	-13.29	1.07	-13.38	0.32

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9