An experimental study of sepiolite dissolution rates and mechanisms at 25 °C

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Abstract

The steady-state dissolution rates of sepiolite were measured as a function of pH from mixed-flow reactor experiments at 25 °C in both citrate bearing and citrate-free aqueous solutions. Dissolution at pH ≤5.5 and pH ≥9.18 was found to be non-stoichiometric, with relatively more Mg being released at low pH, while Si was preferentially released at high pH. The steady-state dissolution rate of sepiolite at 25 °C, based on Si release rates at far from equilibrium conditions, r_+ in mol/cm²/s at pH ≥4.44 can be described by

$$r_+ = 10^{-15.291} (a_{\text{H}^+}^2 / a_{\text{Mg}^{2+}})^{1/8},$$

where a_i refers to the activity of the subscripted aqueous species. This rate equation is based on a dissolution mechanism by which interstitial Mg is exchanged for 2 H⁺, followed by the rate limiting release of partially detached Si-tetrahedra. At pH ≤4.44 and in citrate-free aqueous solutions, sepiolite dissolution rates based on Si release are similar to those measured for amorphous SiO₂ despite the fact that the bulk fluid phase was undersaturated with respect to this solid. In contrast, in citrate bearing aqueous solutions, the Si release rate increases with decreasing pH following a trend consistent with the corresponding higher pH values. This difference is attributed to the increase of amorphous SiO₂ dissolution rates in citrate bearing aqueous fluids, preventing the

formation of substantial SiO₂-rich surface layers. To further examine the extent of non-stoichiometric dissolution and its implications on solid phase transformations, batch experiments were performed in citrate bearing aqueous solutions at pH 2.57, 3.40 and 4.31. During these longer term experiments the fluid phase attained saturation with respect to amorphous SiO₂. From mass balance calculations, Energy-Dispersive X-ray spectroscopy (EDS) and X-Ray powder Diffraction (XRD), it can be inferred that after 688 hours, 98% of the Mg was removed from the solid structure during pH 2.57 batch experiments, while SiO₂ was retained in an amorphous solid phase, demonstrating the independence of the Mg compared to Si release to the aqueous solution.

1. Introduction

Sepiolite is a Mg-rich 2:1 trioctahedral clay, characterized by its continuous inverted tetrahedral sheets and discontinuous octahedral sheets, creating a unique ribbon-like structure (Cornejo and Hermosin, 1988; see Figure 1). Although Mg-rich 2:1 trioctahedral clays are relative scarce on the Earth's surface, sepiolite is found in natural low temperature systems (Guggenheim and Krekeler, 2011), including near submarine hydrothermal vents, in lake deposits, in volcanic deposits and in geothermal systems, including the CarbFix Hellisheidi CO₂ storage pilot site (Arranz et al., 2008; Bowles et al., 1971; Gislason et al., 2010; Perraki and Orfanoudaki, 2008; Stoessell and Hay, 1978; Tutolo and Tosca, 2018). Over the past decade sepiolite has received increased interest as it is been speculated to be one of the few clay minerals that readily precipitates at Earth's surface conditions, thereby directly affecting the Mg and Si availability in some surface waters (Baldermann et al., 2018; Tosca and Masterson, 2014; Tutolo and Tosca, 2018). There are, however, currently no available data on sepiolite dissolution rates and mechanisms as a function of pH.

There are several motivations for this study of sepiolite dissolution. First, it is anticipated that this study will provide further insight into the dissolution mechanisms of the divalent metal-silicate minerals in general. Notably, Me²⁺-silicate dissolution has been observed to be initially non-stoichiometric (cf. Oelkers and Schott, 2001; Saldi et al., 2007; Schott et al., 2012a; Thom et al.,

2013). Relatively more Me^{2+} is released from divalent metal silicate minerals compared to Si at low pH during the initial dissolution of the mineral. This observation has either be attributed to an interface coupled dissolution-precipitation mechanism, or alternatively to the preferential release of Me^{2+} over Si (e.g. Hellmann and Tisserand, 2006; Luce et al., 1972; Oelkers et al., 1994; Ruiz-Agudo et al., 2012; Saldi et al., 2007; Schott et al., 2012). The study of sepiolite dissolution may also provide insight into potential carbon capture and storage processes. The release of Mg^{2+} from silicate minerals can provide the divalent metals for carbon-dioxide mineralization into magnesite, hydromagnesite, nesquehonite, and dypingite (cf. Hamilton et al., 2016; Harrison et al., 2012; Oelkers et al., 2008).

2. Theoretical framework

Sepiolite dissolution can been described by the following reaction (Stoessell, 1988):

The standard state adopted in this study for solutes is that of unit activity of the species in a hypothetical 1 molal solution at infinite dilution at any temperature and pressure. The standard states of H_2O and pure minerals are taken to be 1. Taking account of these standard states, the law of mass action of reaction 1 is given by

$$K_{\text{sepiolite}} = \frac{a_{\text{Mg}^{2+}}^4 a_{\text{SiO}_2}^6}{a_{\text{H}^+}^4} \quad (2)$$

where $K_{\text{sepiolite}}$ designates the equilibrium constant of reaction 1 and a_i refers to the activity of the subscripted aqueous species. All thermodynamic calculations in this study were performed using PHREEQC.v4 (Parkhurst and Appelo, 2013) together with its the Iln database after adding to it the

equilibrium constant for the sepiolite dissolution reactions reported by Stoessell (1988), $\log K_{sepiolite} = 15.76 \pm 0.18$. Note that Voigt et al. (2018) demonstrated that PHREEQC and its Ilnl database accurately calculates the saturation index of amorphous SiO_2 at the conditions considered in this study.

The saturation index (SI) of a mineral can be computed by:

$$SI = \text{LOG}\left(\frac{IAP}{K_{sepiolite}}\right) \quad (3)$$

where IAP refers to the ion activity product, which is defined as the product of the measured activities in reaction 1; e.g. the right hand side of Eq. (2).

In accord with the principle of detailed balancing, surface reaction-controlled dissolution rates can be considered to be the difference between the forward rate (r_+) and the reverse rate (r_-) such that

$$r = r_+ - r_- = r_+ \left(1 - \frac{r_-}{r_+}\right) \quad (4)$$

Note that Eq. (4) is equivalent to (Aagaard and Helgeson, 1982, 1977; Lasaga and Kirkpatrick, 2018; Oelkers and Schott, 1995)

$$r = r_+ (1 - \exp(-A/\sigma RT)) \quad (5)$$

where σ stands for Temkin's average stoichiometric number equal to the ratio of the rate of destruction of the activated or precursor complex relative to the overall dissolution rate, A refers to the chemical affinity of the dissolution reaction, R denotes the gas constant and T designates absolute temperature. All dissolution rates in the present study were measured at far-from-equilibrium conditions, such that $A \gg \sigma RT$. At these conditions $r_- \ll r_+$ and thus $r \approx r_+$. Consequently, sepiolite dissolution rates in this study are thus symbolized r_+ .

Equations describing the variation of r_+ as a function of aqueous solution composition can be obtained through the consideration of transition state theory, which formalizes the relationship between an activated, or precursor complex and the reaction rate. The activated complex is defined

as the chemical configuration of the system at the energy maximum of the reaction path. The precursor complex is related to the activated complex via (Oelkers, 2001; Oelkers et al., 1994; Wieland and Stumm, 1992):

The rate of the reaction is then proportional to the concentration of activated or precursor complexes such that

$$r_+ = k_+[P^*] \quad (7)$$

where k_+ refers to a rate constant and $[P^*]$ is the concentration of the precursor complexes. The reaction creating the precursor complex can be identified from the mineral dissolution mechanism, which proceeds via the breaking of metal-oxygen bonds. The dissolution rate of a multi-oxide mineral is limited by the slowest breaking bond required to destroy the mineral structure. In general, the surface species that contains the slowest breaking bond within the dissolution mechanism is identified as the precursor complex.

The dissolution mechanism of sepiolite can be hypothesized from the dissolution mechanisms of other Mg-silicates. A preferential release of Mg^{2+} under acidic conditions is indicative of a mechanism in which Mg^{2+} is first rapidly exchanged with protons and released from the mineral structure. Subsequently the Si-O structure may partially collapse and eventually break. The exchange reaction of structural Mg^{2+} ($>\text{Mg}$) with two protons, can be expressed by the following reaction:

The partially detached Si tetrahedral resulting from the exchange of H^+ with the structural Mg^{2+} , form the precursor complex. The concentration of partially detached Si tetrahedra can be estimated by combining the law of mass action of reactions (1) and (8). This, together with Eq. (7), yields (cf. Diedrich et al., 2014; Oelkers and Schott, 2001):

$$r_+ = k_+[> \text{Si}^*] = k_+ \left(\frac{K_E \left(\frac{a_{\text{H}^+}^2}{a_{\text{Mg}^{2+}}} \right)^{1/n}}{1 + K_E \left(\frac{a_{\text{H}^+}^2}{a_{\text{Mg}^{2+}}} \right)^{1/n}} \right) \quad (9)$$

where $[> \text{Si}^*]$ denotes the concentration of partially detached Si tetrahedral at the sepiolite surface, and K_E defines the equilibrium constant of the proton exchange reaction (8). The number of partially detached Si tetrahedra formed by the exchange of one Mg^{2+} for 2 H^+ is given by n .

When there is sufficient Mg^{2+} remaining on the dissolving sepiolite surface, Eq. (9) reduces to

$$r_+ = k_+ \left(\frac{a_{\text{H}^+}^2}{a_{\text{Mg}^{2+}}} \right)^{1/n} \quad (10)$$

The validity of equations (9) and (10) will be assessed in this study through the measurement of sepiolite dissolution rates as a function of aqueous solution composition.

3. Materials and methods

3.1. Sepiolite

Two samples of Valdemore, Spain sepiolite were obtained from the Clay Mineral Society. This clay was ground using an agate mortar and pestle. The resulting powder was sieved to obtain the < 63 μm size fraction. This size fraction was cleaned in 5 washing cycles. During each washing cycle the clay was suspended in ethanol, placed in an ultrasonic bath for 5 min, then left to settle for 10 minutes. The overlying suspension was discarded prior to the subsequent washing cycle. The cleaned clay was then dried at 50 °C for 24 hours. The surface area of the ground and cleaned clay sample was measured using Brunauer-Emmet-Teller (BET) theory (Brunauer et al., 1983) from N_2 adsorption measurements, using a Quantachrome Autosorb iQ₂. The resulting surface area of sample one was found to be 236.3 $\pm$ 10% m^2/g , while that of sample two was found to be 214.0 $\pm$ 10% m^2/g . X-ray diffraction (XRD) analysis, using a PANalytical, X'pert PRO MPD, indicated that both samples were pure sepiolite; any impurities in the samples were the below detection limit of ~2 volume percent. As obtained from X-Ray Fluorescence measurements (PANalytical PW 2404), the

sepiolite atomic Mg:Si ratio of the samples was measured to be 3.34:6 ($\pm 5\%$), with traces of Al and Fe (< 0.95 atom%), such that the chemical formula of the sepiolite is consistent with $\text{Mg}_{3.34}\text{Si}_6\text{O}_{15}(\text{OH})_{1.8} \cdot 6\text{H}_2\text{O}$.

3.2. Flow through reactor experiments

Sepiolite dissolution rates were determined from flow through experiments as described by Oelkers and Schott (2001). The flow reactors were constructed from 250 mL Azlon beakers, fitted with custom made lids that allowed for the inflow and outflow of aqueous solutions. A schematic illustration of the reactor is provided in appendix 1. The aqueous solution was pumped through the reactor with a Gilson peristaltic pump that allowed for a constant fluid flow and a wide range of flow rates. To ensure that the sepiolite remained in the reactor during the experiments, a slurry of sepiolite, prepared from 1 g sepiolite and 3 g of inlet solution, was added to a 12-14 kD Visking® dialyses tube. The dialyses tube was closed with a floating closure on one end and a magnetic closure on the other end. The latter allowed for constant stirring of the sepiolite using a magnetic stir plate located under the reactor. The inlet aqueous fluid flowed a constant rate until steady-state was reached and the aqueous Si and Mg concentrations in the outlet solution remained stable within analytical uncertainty over at least 5 residence times; the residence time is defined as the fluid flow rate divided by the reactor volume.

For each experiment, 9 L of inlet aqueous solution was prepared in a Low-Density Polyethylene (LDPE) plastic collapsible bag. Aqueous solutions, with a pH ranging from 1.7 to 10 and having a fixed ionic strength of 0.02 mol kg^{-1} were prepared. The compositions of all inlet solutions are provided in Table 1. The compositions of the citrate-free aqueous inlet solutions used in this study were originally reported by Saldi et al. (2007). Several other experiments were performed in aqueous citrate bearing buffer solutions. All chemicals used to create these reactive aqueous solutions were of analytical grade.

Approximately 10 mL of reactive aqueous solution was collected at regular times from the outlet of the flow reactors during each experiment. The pH of these samples was measured immediately, and the samples were subsequently filtered with a 0.22 µm PES (Hydrophillic Polyethersulfone) Millex® syringe filter. One aliquot of each sample was acidified to 1% v/v HNO₃, using distilled 97% HNO₃ and another aliquot was either acidified or alkalified to a pH of roughly 7, using either distilled 97% HNO₃ or reagent grade 1M NaOH. The aliquots acidified to 1% v/v HNO₃ were analysed for Mg concentration on an Inductive Coupled Plasma – Optimal Emission Spectrometer (ICP-OES). The other aliquots were used for Si analysis. The Si concentrations of P-free fluid samples were obtained from the molybdate blue method (Knudson et al., 1940), using an AA3 HR SEAL Segmented Flow Analyser (SFA). The reproducibility of the Si measurements obtained on the SFA was ±0.1%. When PO₄ was present in the sampled fluids, the Si concentrations were measured by ICP-OES. The reproducibility of the ICP-OES measurements was ±2.6% for Mg and ±3.0% for Si. The dissolution rates of sepiolite were calculated from the measured aqueous fluid steady-state concentrations of Mg and Si, as indicated by a constant outlet Si and Mg concentration, and the fluid flow rate during the experiments using:

$$r_+ = \frac{\Delta m_i * F}{v_i * SSA * M} \quad (11)$$

where Δm_i corresponds to the change in concentration of the i th element between the inlet and outlet solution at steady-state, F stands for the flow rate during the experiment, v_i refers to the stoichiometric number of moles of element i in the dissolving sepiolite, SSA denotes the BET specific surface area of the initial sepiolite and M the mass of sepiolite initially present in the reactor.

3.3. Batch experiments

Batch experiments were performed to illuminate the dissolution mechanism and the extent of non-stoichiometric sepiolite dissolution at low pH. These batch experiments were run in distinct series. Each series consisted of 7 individual batch experiments run with a single initial reactive fluid for a selected time duration. At the end of each individual experiment the reactor was opened and

both the reactor fluid and solid was collected. These experiments could thus provide insights on how the chemical compositions and structure of sepiolite changed due to non-stoichiometric dissolution over specific reaction times.

Three series of batch experiments were run; the compositions of the initial fluids of these experiments are provided in Table 2. The initial reactive aqueous solutions were prepared from analytical grade chemicals and contained aqueous citric acid and phosphate to buffer their pH. Each batch experiment was started by adding 50 mL of the initial aqueous solution and 0.1 g of prepared sepiolite to 60 mL Nalgene High-density polyethylene (HDPE) bottles. The bottles were consequently sealed and placed into a constantly shaking 25 °C water bath.

At preselected time steps an individual batch experiment was stopped. 10 mL of the aqueous solution was collected from the batch reactor and the solution was filtered through a 0.22 µm nylon syringe filter and acidified to 1% v/v HNO₃ using distilled HNO₃. The solids in the reactor were collected by vacuum filtration using a 0.22 µm nylon filter. To remove any solutes from the solid surfaces, the samples were flushed with ethanol immediately after filtering.

The magnesium and silica concentrations of the collected fluids were measured by ICP-OES and the collected solids were analysed with XRD, Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS). The saturation indices of all collected reactor fluids were assessed using PHREEQC.

Dissolution rates of sepiolite were computed from the batch experiments, using:

$$r_+ = \frac{W}{v_i * SSA * M} \left(\frac{\partial C_i}{\partial t} \right) \quad (12)$$

where C_i refers to the concentration in solution, W represents the total mass of aqueous solution added to the reactor and t refers to time. The parenthetical term in Eq. (12) was generated from a linear regression of concentrations measured before each batch reactor series attained saturation with respect to amorphous SiO₂ (see Figure 5).

4. Experimental results

4.1. Flow through experiments

A summary of the experimental results can be found in Table 3, which lists the steady-state outlet fluid compositions, as well as the computed release rates of both Si and Mg, and the saturation indices of these outlet solutions with respect to sepiolite and potentially forming secondary phases. Note that the calculated chemical saturation indices for talc and chrysotile are positive suggesting that these minerals are supersaturated in the flow through experiment run in inlet solutions having a pH of 9.65.

Representative examples of the temporal evolution of the aqueous solution composition during the citrate-free flow-through sepiolite dissolution experiments at pH 1.83, 7.16, and 9.18, and the citrate bearing experiment with an effluent pH of 2.60 are provided in Figure 2. In both the citrate-free experiments and the citrate bearing experiments, the initial rapid release of Mg followed by a decrease in Mg concentrations, after which the concentrations stabilize, and the system reaches a constant steady-state outlet concentration. The Si concentrations at acidic conditions increase linearly at the onset of the experiments and rapidly stabilize, attaining a steady-state well before the corresponding aqueous Mg concentrations. In contrast at circum-neutral and alkaline pH conditions, the aqueous Si concentrations follow a similar temporal evolution to that of Mg.

Steady-state sepiolite dissolution rates from citrate-free experiments (Figure 3) were calculated from the steady-state Si and Mg concentrations, using Eq. (11). Note that while the dissolution rates based on Mg are linearly dependent on the pH, the rates based on Si concentrations deviate from this linear trend in the citrate-free experiments. Figure 2 shows, that at neutral to basic pH, the rates based on Si release increase linearly with decreasing pH. At acidic pH the rates based on Si release in the citrate-free experiments decrease before increasing again. Additionally, the aqueous solution composition trends in Figure 2 confirm the incongruent dissolution of sepiolite at both low and high pH. It is evident, however, that the degree of non-stoichiometric dissolution at acidic conditions is less for the citrate bearing flow experiments (Figure 4) compared to the citrate-free experiments.

In Figure 4, the logarithms of all measured sepiolite dissolution rates based on Si release are plotted as a function of $\log(a_{\text{H}^+}^2/a_{\text{Mg}^{2+}})$. The logarithm of these rates plot as a linear function of $\log(a_{\text{H}^+}^2/a_{\text{Mg}^{2+}})$ with the exception of the rates measured in citrate-free experiments at $\log(a_{\text{H}^+}^2/a_{\text{Mg}^{2+}}) > -0.5$. The linear regression of this data yields the following equation:

$$r_+ = k_+[\text{Si}^*] = 10^{-15.291}(a_{\text{H}^+}^2/a_{\text{Mg}^{2+}})^{1/8} \quad (13)$$

where rates are in units of $\text{mol cm}^{-2} \text{s}^{-1}$. A close correspondence between the measured rates and the regression curve is evident in Figure 4.

4.2. Batch experiments

Batch dissolution experiments were performed to gain further insight into the mechanism of sepiolite dissolution at acidic pH. Table 2 gives the calculated release rates of both Mg and Si during the initial part of each series, as well as the measured fluid compositions and the computed saturation indices of secondary minerals in the reactive fluids collected after the longest experiment of each series. The fluid composition and saturation indices of all the experiments for the three pH conditions are provided in Appendix 2. PHREEQC calculations indicate that amorphous SiO_2 became saturated in the batch experiments after 194 h in the pH 2.57 and 3.50 batch experiments and after 358 h in the pH 4.31 experiments. After this time the reactive fluid Si concentrations remained close to constant and close to equilibrium with respect to amorphous SiO_2 (Table 2, Figure 5). Table 2 also provides the pH at the start of the experiments; as the fluid pH was buffered by the presence of citric acid in the reactive fluids, it remained stable over the course of the experiments. Note that the release rates of both Mg and Si in the batch experiments, prior to the attainment of amorphous SiO_2 saturation, are somewhat faster compared to the corresponding flow through experiments (see Tables 2, 3, Figure 4).

Figure 5 provides both the aqueous solution compositions as well as the percent of the Si and Mg originally in the sepiolite removed from the solid during each batch experiment. Note that at pH 2.57, ~98% of the Mg was removed from the mineral structure after 688 hours, while no more than

20% of the Si was removed. In contrast, at pH 4.31, only 43% of the Mg was removed from the mineral structure, after 688 hours while 20% of the Si was removed. Notice that in all three batch experimental series, the percentage of Si removed from the mineral structure never exceeded 20%.

The preferential removal of Mg from the sepiolite structure is reflected in the EDS results on the solids recovered from the batch experiments. Table 4 provides the results of the EDS analyses and indicates how the Mg content of the dissolving sepiolite decreases over time, with notably the least Mg is left in the pH 2.57 sample recovered after 688 hours. The EDS results reflect a nearly complete Mg removal from this sample and are thus confirm the aqueous solution data observations.

The SEM images (Figure 6) indicate that the needle-like structure of sepiolite is preserved over time in the batch experiments, although the morphology of the needles appears somewhat altered. The needle-like structure of the sepiolite limits the quantification of morphology and crystal size changes in these samples. Although the SEM images (Figure 6) show that the mineral form has been retained, the XRD results indicate that over time the solid loses its original mineral structure such that after 688 hours at pH 2.57 the solid is amorphized. The loss in XRD peak intensities over time suggest the disintegration of the original sepiolite structure (Figure 7).

5. Discussion

5.1. The temporal evolution of the aqueous solution chemistry during the flow through experiments

An initial non-linear temporal Si and Mg release during sepiolite dissolution is observed at the onset of the experiments, where relatively more Si is released under alkaline conditions compared to acidic conditions, while relatively more Mg is released under acidic conditions (see Figure 2). A similar initial non-stoichiometric dissolution has also been observed in talc and enstatite (Oelkers and Schott, 2001; Saldi et al., 2007). Oelkers and Schott (2001) attributed the initial non-stoichiometry in enstatite dissolution experiments to a Mg for proton exchange reaction, due to the

relative bond strength of Si-O and Mg-O as a function of pH (Brantley et al., 2008; Fenter and Sturchio, 2004, Oelkers 2001).

Oelkers et al. (2009) noted that the duration of the non-stoichiometric dissolution of enstatite, diopside and forsterite is different to that observed in wollastonite. Although the dissolution of these former divalent metal-silicates at acidic pH is non-stoichiometric at the onset of the experiment, a steady-state divalent metal depletion depth is attained in flow experiments after several hours to weeks depending on the pH, after which dissolution continues stoichiometrically (Golubev et al., 2005; Oelkers, 2001; Oelkers and Schott, 2001; Pokrovsky and Schott, 2000). In wollastonite however, a steady-state Ca depletion depth might never be attained under acidic conditions (Schott et al., 2012, 2002), similar to the behaviour observed during sepiolite dissolution (see Figure 2). The continuous non-stoichiometric dissolution of wollastonite has been associated with its mineral structure, as Ca can be continuously released through large channels via metal for proton exchange without breaking the Si-O bonds (Schott et al., 2012). We propose that large channels also facilitate the continuous release of Mg from dissolving sepiolite at acid conditions, without breaking the Si tetrahedral sheets by Mg for proton exchange.

5.2. Dissolution rates and mechanisms as a function of pH

Traditionally the dissolution rates of divalent metal silicates as a function of pH have been computed from the release rate of Si as the breaking the Si-bonds is considered to be the slowest step in the dissolution of a silicate mineral (e.g. Bales and Morgan, 1985; Oelkers and Schott, 2001; Saldi et al., 2007; Thom et al., 2013). At alkaline conditions, however, the release of Si from sepiolite is faster than that of Mg suggesting that the breaking of Si-bonds is no longer the slowest step in the dissolution process. Equally, at acidic pH conditions, sepiolite dissolution is non-stoichiometric, as Mg is preferentially released over Si. Hence Si release rates may not be representative of the dissolution rate of sepiolite at all conditions. It seems therefore ambiguous to attribute the dissolution rate of sepiolite to the release rate of either Mg or of Si.

The dissolution rates based on either Mg or Si release of sepiolite as measured in the flow through experiments are comparable to those of talc, anthophyllite and chrysotile, but are considerably lower than the dissolution rates of olivine minerals and Ca-bearing silicates (see Figure 8). Oelkers (2001) and Schott et al. (2009) attributed the relatively rapid dissolution rates of the olivines at acidic conditions to their structure (see also Oelkers et al., 2018). The dissolution of olivine requires only the breaking of relatively weak divalent metal-oxygen bonds, whereas the dissolution of phyllosilicates requires the additional breaking of Si-O bonds. The relatively fast dissolution rates of wollastonite is evidence that Ca-O bonds break relatively rapidly compared to Mg-O bonds (c.f. Schott et al., 1981; Westrich et al., 1993; Oelkers 2001; Schott et al, 2009).

The dissolution rates of sepiolite are nevertheless somewhat faster than those of talc, despite their chemical similarities (Figure 8). This difference can be attributed to the differences in the structures of these two minerals. The discontinuous octahedral sheets in sepiolite create large channels (Figure 1) facilitating the exchange of H^+ with Mg^{2+} , thereby promoting the dissolution of this mineral.

Additionally, a dissolution mechanism by which sepiolite dissolves via Mg removal from the channels rather than the structural sheets can be inferred from the n value in the dissolution rate equation (13). The n value of 8, in rate equations (9) and (10) obtained for sepiolite dissolution contrasts to that found for other 2:1 Mg phyllosilicates; the value of n reported for talc (Saldi et al., 2007) was 4. The n value in dissolution rate equation has previously been associated with the number of structural Si that are partially detached upon exchange of one Me^{2+} from the structure during mineral dissolution. An n value of 8 thus suggests that 8 partially detached Si-rich precursor complexes are formed upon the exchange of one Mg with H^+ . Estaban-Cubillo et al. (2008) proposed that during sepiolite leaching 70% of the Mg removed was Mg positioned at a channel site. At the channel sites the Si/Mg ratio is 6:1, which is higher compared to the 4:1 Si/Mg ratio at the edge of the mineral structure. The preferential removal of Mg from the channel site could therefore account for the relative high n value compared to that for talc (Saldi et al., 2007). That sepiolite dissolution

predominantly proceeds via the initial liberation of Mg from the channels in this mineral can also be inferred from the XRD results (Figure 7) in which, most notably, the peak at a 2θ of 8.46 degrees decreases over time. A decrease in this peak has been associated with a disturbance in the parallel array of the mineral structure (Cornejo and Hermosin, 1988) and thus implicates the disintegration of this channel-like structure.

Figure 3 indicates that at $\text{pH} \leq 4$ the sepiolite Si release rates in aqueous citrate-free solutions match closely to those of amorphous SiO_2 and biogenic phytoliths (microscopic opal). Both sepiolite Si release and biogenic phytoliths dissolution, show a minimum as a function of pH at approximately pH 2.8 (Frayssé et al., 2006). The average $\log(r_+)$ of sepiolite at pH 1.8-4.22 is $-16.28 \text{ mol/cm}^2/\text{s}$, whereas that of biogenic phytoliths is $-16.23 \text{ mol/cm}^2/\text{s}$ (Frayssé et al., 2006). This similarity suggests that the solid structure remaining upon the release of Mg from sepiolite in the absence of aqueous citrate is similar to that of amorphous SiO_2 . The formation of amorphous SiO_2 during these sepiolite dissolution experiments is confirmed by the EDS (Table 4) and XRD data (Figure 7). Schott et al. (2012) previously reported similar observations of the long-term (>2000 h) dissolution of wollastonite; they report long-term wollastonite dissolution rates that are intermediate between those of phytoliths and quartz. The similarities in the dissolution rate of wollastonite with those of quartz and phytoliths were attributed to the extensive hydrolysis and condensation of the silanol groups, which followed the Ca^{2+} for H^+ exchange reaction.

Silicon release rates at acidic conditions are notably faster in the citrate-bearing compared to the citrate-free reactive fluids (Table 2 and 3, Figure 4). This difference may stem from the effect of the presence of aqueous citrate on amorphous SiO_2 dissolution rates. The addition of aqueous citrate increases the dissolution rates of any amorphous SiO_2 formed upon the initial release of Mg from the crystal structure (c.f. Bennett et al., 1988). Bennett (1991) reported a 10-fold increase in quartz dissolution rates upon the addition of 0.2 mol/L K-citrate at pH 7. Additionally, dissolution rates were found to increase linearly with increasing K-citrate concentration (Bennett, 1991). The observed increase in sepiolite dissolution rates due to the presence of citrate in the fluid phase is

thus consistent with the conclusion that the Si-release rate reflects the dissolution of amorphous SiO_2 formed upon Mg release. Note also that the similarities in the Si release rates determined in citrate-bearing aqueous solutions measured in the batch experiments and the flow through experiments validates the experimental design and confirms that the use of dialysis tubing has no impact on the measured dissolution rate.

The rate equation for sepiolite dissolution (Eq. 13) accurately describes the dissolution of sepiolite rates at pH 2.6 and 3.6 measured in the citrate bearing flow through experiments, whereas it overestimates considerably the Si release rates at $\text{pH} \leq 4.44$ in the citrate-free flow through experiments. In citrate-free flow experiments we postulate that amorphous SiO_2 forms upon the release of Mg from the sepiolite structure, hence the Si release rates reflect the dissolution of amorphous SiO_2 rather than the dissolution rates of sepiolite. Aqueous citrate, however, increases Si release rates, thereby preventing the formation of thick amorphous SiO_2 layers. In such cases the Si release rates appear to reflect the dissolution of sepiolite rather than dissolution rates of formed $\text{SiO}_2(\text{am})$.

The dissolution rates, based on Si release determined in the batch experiments reported in this study also closely match those generated using Eq. (13). Note the rates reported in this study from the batch experiments are based only on the Si release rates before the reactive fluids attained saturation with respect to amorphous SiO_2 . As such it seems reasonable to conclude that a $\text{SiO}_2(\text{am})$ layer had yet to form on these sepiolite surfaces. As can be seen in Fig. 5, over the long-term the aqueous fluid compositions closely match those in equilibrium with $\text{SiO}_2(\text{am})$. This observation as well as the XRD patterns of the solids collected from these batch reactors suggest that $\text{SiO}_2(\text{am})$ formed on the sepiolite surfaces reacted during the batch experiments over longer time durations.

5.3. Non-stoichiometric dissolution at alkaline conditions

Similar to previous observations during talc (Saldi et al., 2007), olivine (Pokrovsky and Schott, 2000), and chrysotile (Bales and Morgan, 1985) dissolution, sepiolite dissolution becomes

incongruent at pH >9.25 due to preferential Si release. This observation has been attributed to either the precipitation of Mg-rich secondary phases (Saldi et al., 2007) or to the preferential leaching of Si. The latter can be explained by a similar mechanism as proposed for the preferential removal of Mg under acidic conditions; under alkaline conditions, the Si-O bonds break relatively fast compared to the Mg-O bonds. Such a mechanism is consistent with the relative dissolution rates of amorphous SiO₂ compared to those of brucite (Mg(OH)₂) at pH >10, with the dissolution rates of brucite, reflecting the rate of breaking Mg-O bonds, being slower than those of amorphous SiO₂ at these alkaline conditions (Frayssé et al., 2006; Oelkers et al., 2018; Pokrovsky and Schott, 2004). The difference in dissolution rates between brucite and amorphous SiO₂ could be due to the protonation of the mineral surfaces as a function of pH, as the point of zero charge of brucite lies at pH 11 (Pokrovsky and Schott, 2004), while that of amorphous SiO₂ lies at pH 2 (Parks, 1967). Hence, at pH >10 unreactive >MgOH⁰ dominates the brucite surface, while relatively reactive deprotonated >SiO⁻ sites dominate amorphous SiO₂ surface at this pH. Deprotonated sites have a greater tendency for hydrolysis and thus to promote mineral dissolution (Nangia and Garrison, 2008). Additionally, the exchange reaction of >Mg with H⁺ is less favourable under alkaline conditions, compared to acidic conditions, due to the low concentration of protons at high pH (cf. Oelkers et al., 2009).

Geochemical calculations suggest that the non-stoichiometric dissolution of sepiolite at pH >9.18, does not result from the precipitation of a Mg-rich secondary phase, as suggested by Saldi et al. (2007) for the case of talc. Although, PHREEQC calculations suggest that the bulk aqueous solution in the pH 9.65 dissolution experiments is saturated with respect to talc and chrysotile, these phases do not precipitate under ambient conditions. Tosca et al., (2011) reported that the precipitation of (amorphous) Mg-silicates at ambient temperatures requires a fluid saturation state of greater than 17 with respect to chrysotile and talc. An alternative interpretation of such observations stems from interface coupled dissolution precipitation. This mechanism has been proposed to facilitate the precipitation of secondary phases in locally supersaturated but overall undersaturated aqueous solutions (Ruiz-Agudo et al., 2014, 2012). If all the non-stoichiometric retention of Mg was attributed

to brucite precipitation, the mass of brucite precipitated can be determined from mass balance calculations. The results of this calculation suggest that no more than 0.53 wt.% of the mass of solid recovered at the end of the flow through experiment at pH experiment 9.67 was brucite. This small mass would be undetectable using the techniques used in this study.

5.4. Non-stoichiometric sepiolite dissolution at acidic conditions

Steady-state sepiolite dissolution at acidic conditions is non-stoichiometric as Mg is preferentially released to the fluid phase throughout the batch and flow experiments (Figures 2, 3 & 5). This behaviour is consistent with the relative rates of breaking the divalent metal-oxygen bonds compared to the Si-O bonds in these mineral structures (cf. Oelkers, 2001; Oelkers et al., 2009), where divalent metal-oxygen bonds break with relative ease compared to the Si-O bonds. Although talc (Saldi et al., 2007), chrysotile (Thom et al., 2013), oligoclase (Stillings and Brantley, 1995), diopside (Golubev et al., 2005), tremolite (Diedrich et al., 2014), and labradorite (Sjoberg, 1989) also display non-stoichiometric dissolution, the non-stoichiometric dissolution behaviour of these minerals is limited to the onset of the dissolution experiment, upon which dissolution becomes stoichiometric when the experiments reach steady-state. The difference in the acid dissolution behaviours of these minerals is likely related to the ease at which the divalent metals and hydrogen can be transported through the metal depleted surface layer. In sepiolite, the discontinuous octahedral sheets allow for the transport of Mg and H through the altered mineral surface structure into the aqueous solution.

The observations presented above suggest a mechanism in which non-stoichiometric dissolution of sepiolite at acidic conditions can be attributed to preferential Mg release from the mineral through a proton for divalent metal exchange reaction. This exchange can lead to a collapse of the Si tetrahedra and subsequent hydrolysis and condensation depending on fluid composition. This mechanism is consistent with both the preferential release of Mg (cf. Luce et al., 1972; Oelkers and Schott, 2001; Saldi et al., 2007; Schott et al., 2012) as well as the measured steady-state release

rates of Si at acidic conditions, which are similar in the absence of aqueous citrate – both in the rate and pH dependency - to those previously measured for biogenic phytoliths (Frayse et al., 2006). In the presence of aqueous citrate at acidic conditions, however, measured Si release rates in open system experiments approach those of Mg, and appear to be consistent with those of sepiolite measured at higher pH. This may be due to the promotion of Si-release by aqueous citrate.

The formation of amorphous SiO₂ layers on dissolving mineral surfaces, resulting in a decreased dissolution rate, has also been reported for other mineral systems. Daval et al. (2011) reported that a thin amorphous SiO₂ layer formed during olivine dissolution, resulting in passivation of the mineral surface and lower dissolution rates. Similar observations were reported by Grambow and Müller (2001), who studied the dissolution behaviour of nuclear waste glass. Both studies, however, ascribe the amorphous SiO₂ layer that formed to the precipitation of amorphous SiO₂ rather than the formation of amorphous SiO₂ via the removal of divalent cations followed by a collapse of the Si tetrahedra.

An alternative approach to describing the non-stoichiometric dissolution of Me²⁺-silicates is based on the concept of interface coupled dissolution precipitation mechanisms (cf. Hellmann et al., 2012; King et al., 2010; Putnis, 1992, 1999; Putnis and Putnis, 2007; Ruiz-Agudo et al., 2012, 2014). Within this approach the initial release of divalent metals and Si is stoichiometric into a local isolated aqueous phase within the metal depleted surface layer. This initial release to this isolated aqueous phase is coupled to a rapid local reprecipitation of a Si-rich phase.

The degree to which the presence of the amorphous SiO₂ like-layer on the sepiolite surface formed due to a dissolution-precipitation mechanism (Putnis, 2009) or a hydrolysis and condensation of the silanol groups (Schott et al., 2012) after Mg for H exchange is somewhat arbitrary. In both cases, the transformation of the sepiolite to an amorphous SiO₂ like-layer occurs deep within the mineral through the 1) breaking of bonds of the original mineral, 2) the transport of Mg from the interface between the original sepiolite surface through the Mg depleted layer to the bulk solution, 3) the transport of hydrogen ions from the bulk solution to this interface, and 4) the

creation of new Si-O-Si linkages. Both mechanisms involve the breaking and reforming of bonds via the intervention of minute quantities of water or hydronium ions, rather than a bulk water phase.

Although a sharp interface between the original mineral and the depleted layer is often considered indicative for a dissolution-precipitation mechanism (c.f. Hellmann et al., 2012), such an interface can also form if the rate of transport of material through the depleted layer is faster than the rate of breaking bonds at this interface. In sepiolite, when Mg is efficiently removed from the interlayer and transported through the mineral structure before secondary collapse of the tetrahedra sheet, there would be no evident diffusion profile in the solid phase. Equally, both mechanisms preserve the original morphology of the original mineral, as observed during sepiolite dissolution.

Non-stoichiometric dissolution of sepiolite at low pH could potentially promote the efficiency of CO₂ sequestration. Water containing abundant CO₂ is acidic (Matter et al., 2009). At such conditions, sepiolite preferentially releases Mg thereby potentially enhances CO₂ sequestration via the mineralization into minerals such as magnesite, hydromagnesite, nesquehonite, and dypingite (cf. Hamilton et al., 2016; Harrison et al., 2012; Oelkers et al., 2008).

5.5. Experimental uncertainties

The uncertainties in the calculated release rates of Si and Mg as well as the computed dissolution rates from the flow through experiments, are associated with the uncertainties in the measured Si and Mg concentration values ($\pm 3\%$ or less), the experimental uncertainties in the pH (± 0.04 pH), the uncertainty in the flow rate ($\sim 4\%$) and the uncertainties associated with the measured surface area ($\pm 10\%$). Hence, assuming that the uncertainties can be exclusively estimated from these contributions, the uncertainty of the computed release rates of Si and Mg is $\sim 15\%$ (~ 0.1 log unit). However, the sepiolite surface area changes upon dissolution, contributing to an additional uncertainty. The contribution of such a surface area change to the measured rate, could be

considerable (Diedrich et al., 2014; Gautier et al., 2001). Such changes can account for some of the scatter in the computed dissolution rates (Figure 4).

6. Conclusion

Dissolution rates of sepiolite were measured at 25 °C at far from equilibrium conditions. Major results of this study include:

- The far from equilibrium dissolution rates based on Si release in the citrate-free flow through experiments at pH >4.44 and citrate buffered experiments at pH <4.4, of sepiolite in units of mol/cm²/s, is consistent with

$$r_+ = 10^{-15.291} (a_{\text{H}^+}^2 / a_{\text{Mg}^{2+}})^{1/8}$$

- The addition of citrate promotes the release of SiO₂ and therefore hinders the formation of extensive amorphous SiO₂ layers at pH <4.44. Under these conditions the citrate bearing experiments appear to represent the dissolution of sepiolite, while in the citrate-free experiments the Si release rates from sepiolite at pH <4.44 reflect the dissolution of SiO₂(am).
- Sepiolite dissolution at acidic conditions proceeds by Mg transport through the channels of the mineral structure, leading to the preferential removal of this metal through a depleted surface layer. This leads the steady-state dissolution of sepiolite to be non-stoichiometric, where Mg is preferentially released over Si. Preferential release of Mg under some conditions is associated with the formation of extensive Si-rich leached layers, which form upon the collapse of the Si-tetrahedra. Under alkaline conditions, Si is preferentially released over Mg. Such preferential released is attributed to differences in the Si-O bonds breaking relatively fast compared to the Mg-O bonds under these pH conditions.

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Table 1: Inlet solution compositions of the flow experiments. The ionic strength of all inlet solutions was 0.02 mol/kg. The composition of the citrate-free inlet solutions were originally computed by Saldi et al. (2012).

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735 Table 2: Initial solution compositions and pH of the batch experiments, as well as the Mg and Si
736 concentrations at the end of the longest experiment of each series; each series ran 688 hours. The
737 final concentration of Si and Mg represent the Si and Mg concentrations in the batch that was
738 sacrificed after 688 hours. The saturation indices of the solutions were computed with PHREEQC.
739 Notice that amorphous SiO₂ approaches saturation during each batch reactor experiment series. The
740 rates (r) of Mg and Si release were calculated from Eq. 12, using the Mg concentrations of the
741 experiments run from between 73 and 688 hours and the Si concentrations from the experiments
742 run between 24 and 193; that is when the concentration change was approximately linear with time
743 and the Si concentrations continuously increased.

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<i>pH^a</i>	<i>Citric Acid g/L^a</i>	<i>Na₂PO₄ g/L^a</i>	<i>Mg (final) mmol/kgw</i>	<i>Si (final) mmol/kgw</i>	<i>log r₊ (Mg)^a mol/cm²/s</i>	<i>log r₊ (Si)^c mol/cm²/s</i>	<i>SI Brucite (final)</i>	<i>SI Talc (final)</i>	<i>SI Anthophyllite (final)</i>	<i>SI SiO₂(am) (final)</i>	<i>SI Chrysotile (final)</i>	<i>SI Sepiolite (final)</i>
2.56	18.4	3.02	10.41	3.578	-15.21	-15.52	-13.03	-21.03	-63.31	0.2954	-26.18	-31.91
3.40	7.12	4.57	7.386	3.586	-15.36	-15.76	-11.81	-17.35	-54.74	0.2973	-22.51	-27.02
4.31	5.59	6.64	4.965	4.009	-15.50	-15.85	-10.52	-13.27	-45.28	0.3457	-18.52	-21.55

a) Initial fluid composition and pH, b) sepiolite dissolution rates based on Mg release, c) sepiolite dissolution rates based on Si release

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<i>pH</i> <i>inlet</i>	<i>pH</i> <i>outlet</i>	<i>Surface</i> <i>area</i> <i>m</i> ²	<i>Outlet Mg</i> <i>mol/kgw*10</i> ⁶	<i>Outlet Si</i> <i>mol/kgw*10</i> ⁶	<i>Fluid flow</i> <i>rate</i> <i>g/min</i>	<i>Log r₊</i> <i>(Mg)</i> ^b <i>mol/cm</i> ² / <i>s</i>	<i>Log r₊</i> <i>(Si)</i> ^c <i>mol/cm</i> ² / <i>s</i>	<i>SI Brucite</i> <i>kJ/mol</i>	<i>SI Talc</i> <i>kJ/mol</i>	<i>SI</i> <i>Anthophyllite</i> <i>kJ/mol</i>	<i>SI</i> <i>SiO₂(am)</i> <i>kJ/mol</i>	<i>SI Chrysotile</i> <i>kJ/mol</i>	<i>SI Sepiolite</i> <i>kJ/mol</i>
1.7	1.83	94.52	28.06	7.740	2.99	-15.41	-16.15	-18.32	-47.55	-121.6	-2.368	-47.373	-69.04
2.3	2.3	123.3	25.08	9.028	3.10	-15.39	-16.27	-16.37	-41.45	-107.5	-2.302	-41.4013	-60.86
2.7	2.8	121.9	23.54	6.930	2.90	-15.38	-16.33	-15.36	-38.88	-101.3	-2.417	-38.6013	-57.51
3.3	3.43	136.8	21.98	7.844	2.46	-15.50	-16.42	-14.11	-34.89	-92.12	-2.363	-34.7255	-52.17
4	4.22	137.5	15.38	1.064	2.79	-15.83	-16.13	-12.23	-28.73	-77.91	-2.230	-28.8262	-43.86
4.7	6.22	122.7	2.149	2.473	2.69	-16.24	-16.31	-10.29	-25.45	-69.42	-2.864	-24.2812	-39.91
7	7.16	162.3	14.52	19.51	0.743	-16.60	-16.63	-6.812	-11.42	-37.86	-1.968	-12.0385	-20.60
7.5	7.31	165.2	10.77	15.59	0.733	-16.66	-16.69	-6.641	-11.29	-37.44	-2.066	-11.7191	-20.50
8	8.02	158.6	9.029	12.08	0.465	-16.76	-16.76	-5.294	-7.581	-28.68	-2.146	-7.8471	-15.61
8.55	8.49	169.0	11.95	18.15	0.434	-16.92	-16.92	-4.236	-3.870	-20.20	-2.013	-4.401	-10.57
9.25	9.18	165.9	5.295	8.992	0.439	-17.25	-17.20	-3.208	-2.225	-15.88	-2.373	-2.0366	-8.615
9.7	9.65	161.9	5.897	16.62	0.237	-17.46	-17.12	-2.225	1.350	-7.745	-2.217	1.226	-3.744
2.60 ^B	2.60	117.3	45.36	23.70	3.541	-15.25	-15.71	-15.50	-37.16	-98.04	-1.883	-37.95	-54.86
3.50 ^B	3.50	109.9	50.07	22.08	2.301	-15.31	-15.80	-13.62	-31.61	-86.05	-1.914	-32.34	-47.49

a) citrate bearing flow through experiments; b) sepiolite dissolution rates based on Mg release, c) sepiolite dissolution rates based on Si release

Table 3: Experimental conditions and results of the flow through experiments. The pH was measured in the outlet fluids and the saturation indexes were computed using PHREEQC. A negative saturation index indicates dissolution is unfavourable, but a positive saturation index indicates the precipitation of the mineral is thermodynamically favourable.

Table 4: Energy-dispersive X-ray spectroscopy (EDS) data for the sepiolite experiments, T3, T5 and T7 terminated after 73, 358 and 688 hours, respectively. The $\pm$ -values represent the 5% uncertainty associated with these measurements. The at.% represents the atomic percentage of the element in the solid phase and the Si/Mg is the atomic ratio of Si/Mg as measured in the solid.

Experimental solid	At.% Mg	At.% Si	At.% O	Si/Mg
<i>Pure Sepiolite</i>	16.54 $\pm$ 0.827	41.56 $\pm$ 2.078	41.90 $\pm$ 2.10	2.51
<i>pH 4.31 T3</i>	14.96 $\pm$ 0.748	33.59 $\pm$ 1.68	51.44 $\pm$ 2.57	2.25
<i>pH 4.31 T5</i>	12.09 $\pm$ 0.605	32.00 $\pm$ 1.60	55.91 $\pm$ 2.80	2.65
<i>pH 4.31 T7</i>	11.64 $\pm$ 0.582	42.10 $\pm$ 2.11	46.26 $\pm$ 2.31	3.62
<i>pH 3.40 T3</i>	13.08 $\pm$ 0.654	25.83 $\pm$ 1.29	61.09 $\pm$ 3.05	1.98
<i>pH 3.40 T5</i>	11.84 $\pm$ 0.692	39.13 $\pm$ 1.96	49.04 $\pm$ 2.45	3.31
<i>pH 3.40 T7</i>	8.670 $\pm$ 0.434	40.07 $\pm$ 2.00	51.26 $\pm$ 2.56	4.62
<i>pH 2.57 T3</i>	16.23 $\pm$ 0.812	41.21 $\pm$ 2.06	42.56 $\pm$ 2.13	2.54
<i>pH 2.57 T5</i>	8.120 $\pm$ 0.406	41.97 $\pm$ 2.10	49.91 $\pm$ 2.50	5.17
<i>pH 2.57 T7</i>	0.4000 $\pm$ 0.020	40.89 $\pm$ 2.08	58.71 $\pm$ 2.94	102.2

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763 Figure 1: Schematic illustration of the sepiolite structure. Note how the tetrahed
764 continuous, while the octahedral sheets are discontinuous, forming channels in
765 structure. These channels hold 'zeolitic water' when the sample is dry and they c
766 transport of Mg and Si from the mineral into the bulk solution during sepiolite dissoluti

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773 Figure 2: Results of selected flow through experiments. Left: Temporal evolution of the fluid Si and

774 Mg concentration; centre the ratio of Si/Mg released during experiments; Right: Temporal fluid pH

775 evolution. Note the spike in the Mg and Si concentrations at the onset of the experiment, after

776 which steady-state dissolution rates are attained, as apparent by the stable concentrations of Si and

777 Mg over time. This figure also shows that dissolution is non-stoichiometric at low pH (pH 1.83), when

778 Mg is preferentially released over Si, while dissolution is approximately stoichiometric at neutral pH

779 (pH 7.16). At high pH (pH 9.18) Si is preferentially released over Mg, resulting in a relatively high
780 Si/Mg ratio compared to stoichiometric release.

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Figure 3: Computed steady-state sepiolite release rates of based on Mg and Si release in citrate-free experiments as a function of pH. The error bars depict a log 0.1 estimated uncertainty on the rates. The dashed line traces the dissolution rates of amorphous SiO_2 , reported Fraysse et al., (2006).

Figure 4: Logarithm of measured steady-state sepiolite dissolution rates based on Si release, as a function of the $\log(a_{\text{H}^+}^2/a_{\text{Mg}^{2+}})$. Error bars correspond to the 0.1 log unit uncertainty associated with the computed dissolution rates. The dashed line represents the regression of the data to Eq. (12) by a least square fit, with a coefficient of uncertainty (R^2) of 0.911. The filled circles correspond to results of the flow experiments performed in and absence of aqueous citrate; the open diamonds represent results of the aqueous citrate-bearing flow through experiments (CB Flow through), the open circles represent the data obtained from the batch experiments performed in citrate-bearing solutions before the fluids attained equilibrium with amorphous SiO_2 . The equation shows the linear data fit Si release rates of the citrate free flow through data at $\log(a_{\text{H}^+}^2/a_{\text{Mg}^{2+}}) < -5$; this fit appears to match closely the rates of sepiolite at lower pH determined from citrate bearing experiments.

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803 Figure 5: Temporal evolution of the fluid phase Mg and Si concentration during the batch

804 experiments (plots on the left) and the percent Mg and Si removed from the sepiolite (plots on the

right). Si and Mg concentrations are normalized to the Mg and Si stoichiometry in sepiolite, by dividing the Si and Mg concentrations by their atomic number in the sepiolite (6 and 3.34 respectively). The dashed line gives the Si concentration in equilibrium with amorphous silica. The data indicates that the Si concentrations stabilize over time and long-term fluid Si concentrations are close to that in equilibrium with amorphous silica. The red line is the linear least square fit of the Si concentrations as a function of time for those data collected before the fluid attained equilibrium with amorphous SiO_2 . The red R^2 gives the coefficient of determination associated with this fit. The blue line represents a linear least square fit of the Mg concentrations as a function of time for those data collected before the fluid attained equilibrium with amorphous SiO_2 . The blue R^2 gives the coefficient of determination associated with the Mg data fit. The error bars correspond to a 5% uncertainty associated with these data. Note that in the batch experiments at pH 2.57, almost all the Mg is removed from the solid, while at pH 4.31 almost 60% is retained in the solid structure during the experiments.

Figure 6: Scanning Electron Microscopy (SEM) images of sepiolite, collected from the pH 2.57 batch experiments of different experiment durations as indicated in the figure. The images indicate how the morphology of the sepiolite changes over time, notably the needles appear larger over time.

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827 Figure 7: X-ray diffraction (XRD) spectra of sepiolite collected from the batch experiments run in

828 aqueous citrate-bearing pH 2.57 solutions of selected durations. The curves labelled T3, T5 and T7

829 represent respectively the results of experiments run 73, 358, and 688 hours. Note the considerable

830 decrease of the peak at 8.46 degrees 2θ over time.

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833 Figure 8: Dissolution rates of selected Ca/Mg silicates at 25 °C as a function of pH. The dashed line
 834 represents the dissolution rates of sepiolite based on Si release as obtained in this study from the
 835 citrate-free experiments at pH > 4 as well as the citrate bearing experiments at pH < 4. This figure is
 836 adapted from Schott et al. (2009).

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841 Appendix 1: Schematic illustration of the reactor system used for the flow through experiments
842 performed in this study. Sepiolite is retained in the reactor within a dialysis tube, sealed by two
843 closures, one of which is fitted with a magnetic stir bar. This allows the dialysis to stir constantly due
844 to the magnetic stir plate located under the reactor

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846 Appendix 2: Summary of the batch reaction pH, solution compositions and saturation indices at each sampled time step.

<i>Batch experiments at pH 2.56</i>									
<i>Experiment duration (h)</i>	<i>pH</i>	<i>Mg (mmol/kgw)</i>	<i>Si (mmol/kgw)</i>	<i>SI Brucite</i>	<i>SI Talc</i>	<i>SI Anthophyllite</i>	<i>SI SiO₂(am)</i>	<i>SI Chrysotile</i>	<i>SI Sepiolite</i>
5	2.56	0.3516	0.1557	-14.96	-32.23	-87.64	-1.064	-34.66	-47.76
24	2.47	0.8998	0.5863	-14.72	-29.21	-81.36	-0.4894	-32.79	-43.35
73	2.68	2.790	2.705	-13.84	-23.94	-69.95	0.1741	-28.85	-35.88
194	2.68	5.377	4.747	-13.57	-22.13	-66.04	0.4185	-27.53	-33.30
358	2.7	7.126	4.326	-13.41	-21.82	-65.28	0.3792	-27.14	-32.92
458	2.85	8.952	3.870	-13.04	-20.91	-63.09	0.3304	-26.13	-31.74
699	2.82	10.41	3.578	-13.03	-21.03	-63.31	0.2954	-26.18	-31.91
<i>Batch experiments at pH 3.40</i>									
<i>Experiment duration (h)</i>	<i>pH</i>	<i>Mg (mmol/kgw)</i>	<i>Si (mmol/kgw)</i>	<i>SI Brucite</i>	<i>SI Talc</i>	<i>SI Anthophyllite</i>	<i>SI SiO₂(am)</i>	<i>SI Chrysotile</i>	<i>SI Sepiolite</i>
5	3.35	0.3017	0.1262	-13.63	-28.63	-79.11	-1.157	-30.87	-43.02
24	3.51	0.6852	0.3428	-13.00	-24.99	-71.20	-0.7220	-28.11	-37.88
73	3.39	1.759	1.404	-12.80	-21.93	-64.87	-0.1099	-26.27	-33.39
194	3.5	4.150	3.695	-12.23	-18.56	-57.57	0.3103	-23.74	-28.62
358	3.64	5.488	4.073	-11.88	-17.32	-54.74	0.3525	-22.59	-26.94
458	3.78	6.492	3.869	-11.58	-16.52	-52.83	0.3303	-21.74	-25.88
699	3.6	7.386	3.586	-11.81	-17.35	-54.74	0.2973	-22.51	-27.02
<i>Batch experiments at pH 4.31</i>									
<i>Experiment duration (h)</i>	<i>pH</i>	<i>Mg (mmol/kgw)</i>	<i>Si (mmol/kgw)</i>	<i>SI Brucite</i>	<i>SI Talc</i>	<i>SI Anthophyllite</i>	<i>SI SiO₂(am)</i>	<i>SI Chrysotile</i>	<i>SI Sepiolite</i>
5	4.3	0.2555	0.1139	-12.18	-24.45	-69.30	-1.200	-26.61	-37.48
24	4.23	0.5543	0.3040	-11.94	-22.02	-64.20	-0.7744	-25.03	-33.96
73	4.28	1.220	1.022	-11.53	-18.68	-57.10	-0.2479	-22.74	-29.15
194	4.43	2.685	2.913	-10.98	-15.22	-49.65	0.2070	-20.20	-24.24
358	4.6	3.951	4.071	-10.60	-13.48	-45.78	0.3524	-18.75	-21.82
458	4.56	4.554	4.158	-10.58	-13.40	-45.60	0.3616	-18.68	-21.71
699	4.58	4.965	4.009	-10.52	-13.27	-45.28	0.3457	-18.52	-21.55