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## Non-stoichiometric dissolution of sepiolite

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### Abstract

Sepiolite is one of the few Mg-phylosilicates thought to precipitate at Earth's near-surface conditions, and in hydrothermal systems. Understanding the dissolution mechanisms of sepiolite can elucidate Mg-silicate dissolution processes in general and can provide a better estimation of the availability of divalent cations for CO<sub>2</sub> sequestration. Batch experiments containing sepiolite were conducted over a pH range of 3.6–10.4, and the changes in Si/Mg ratio in solution were measured over time. The reaction products were analyzed with scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction. Under all conditions sepiolite dissolution proved to be non-stoichiometric, where Mg was preferentially released under acidic and neutral conditions, while Si was preferentially released in alkaline solutions. Under acidic and neutral conditions, sepiolite could thus release ample divalent cations for CO<sub>2</sub> sequestration.

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*Keywords:* Non-stoichiometric dissolution; divalent metal release; sepiolite

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### 1. Introduction

Dissolution and precipitation of Mg-silicates plays an important role in the global Mg cycle [1], impacting the Earth's surface and subsurface water chemistry and ecosystems [2]. Despite being relatively uncommon, sepiolite (Mg<sub>4</sub>Si<sub>6</sub>O<sub>15</sub>(OH) · 6H<sub>2</sub>O), a Mg TOT-clay, is one of the few authigenic Mg-silicates to form under ambient conditions and has been found to precipitate in hydrothermal systems, on the sea floor and in lake sediments [3–6]. Sepiolite precipitation could thus directly affect Mg availability in these environments. Sepiolite has also been found at the CarbFix Hellisheidi CO<sub>2</sub> storage pilot project in Iceland [7], where the release of Mg<sup>2+</sup> could provide divalent cations

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necessary to sequester CO<sub>2</sub>. Understanding the dissolution behavior of sepiolite could thus allow for better quantitative models of CO<sub>2</sub> sequestration.

Additionally, studying the dissolution behavior of sepiolite can provide information on the dissolution processes of divalent metal- (Me<sup>2+</sup>) bearing silicates in general. Previous work on the dissolution of Me<sup>2+</sup>-silicates has shown that under acidic conditions non-stoichiometric dissolution favors the release of Me<sup>2+</sup> over Si [8–11]. Such preferential Me<sup>2+</sup> release is associated with a rapid exchange of Me<sup>2+</sup> with H<sup>+</sup>, after which the remaining Si-O skeleton either disintegrates [8,12] or is preserved as leached layer [9]. Alternatively, it has been postulated that incongruent dissolution of wollastonite (CaSiO<sub>3</sub>) under acidic conditions is driven by interface coupled dissolution-reprecipitation, where Ca<sup>2+</sup> is released, while SiO<sub>2</sub>(s) directly reprecipitates, allowing for the preservation of the initial crystal morphology [13]. In alkaline solutions, the effect of pH on the congruence of dissolution is not as well-constrained. Saldi et al. [8] found that talc dissolution is congruent under alkaline conditions, while during forsterite dissolution in alkaline conditions, Si is preferentially released and a Mg-rich layer is formed [14]. Preferential release of Si from forsterite has been attributed to its crystal structure allowing for the hydrolysis and removal of isolated SiO<sub>4</sub> from the surface [14,15]. Differences in crystal structure could therefore account for the differences in the dissolution behavior. Sepiolite differs in structure from forsterite and talc; the Mg-rich octahedral sheets are discontinuous, while the octahedral Si-sheets are continuous [16]. Studying the dissolution behavior of sepiolite can thus provide insights into the dissolution mechanisms of Mg-silicates as a function of pH and crystal structure.

## 2. Methods

### 2.1. Sepiolite Samples

Sepiolite (SepSp-1), from Valdemore, Spain, was purchased from the Clay Minerals Society. The sepiolite was manually ground and washed in five cycles to remove fines. During each washing cycle, the sepiolite was suspended in ethanol, placed in an ultrasonic bath for five minutes and then allowed to settle for 20 minutes before discarding the overlying suspension. The remaining material was dried at 50 °C overnight. Images collected with scanning electron microscopy (SEM) confirmed that all fines were removed, and X-ray diffraction (XRD) analysis revealed that no impurities were present above the detection limit of approximately 1 wt.%. The elemental composition of the sepiolite was determined by X-ray fluorescence (XRF), providing a Si:Mg ratio of 6:4. The attribution of other components, including Al, Fe, K and P are measured to be ~1.3 at.%. The specific surface area of the clean sepiolite was 236.3 m<sup>2</sup>/g, as measured by N<sub>2</sub> adsorption with the BET method.

Table 1. Initial solution composition of the different dissolution batch experiments

Experiment	Initial pH	Na <sub>2</sub> HPO <sub>4</sub> (g/kg)	C <sub>6</sub> H <sub>8</sub> O <sub>4</sub> (g/kg)	NH <sub>4</sub> Cl (g/kg)	NH <sub>3</sub> (g/kg)
SEPD 3.6	3.60	7.885	12.645		
SEPD 5.6	5.60	16.309	8.739		
SEPD 7.0	7.00			10.506	0.181
SEPD 10.4	10.40			1.647	10.270

### 2.2. Dissolution experiments

Batch experiments (referred to as SEPD) were performed in 500 mL polypropylene Nalgene bottles placed in 25±1 °C shaking water baths. Sepiolite (1.0 g) was added to a pH-buffered solution with a fixed pH and an ionic strength of ~ 0.2 M (Table 1) and all experiments were conducted in duplicate. All solutions were prepared from analytical grade chemicals. At each time step, 2 mL of fluid was collected from each bottle, filtered with a 0.22 μm syringe filter and acidified to 1% HNO<sub>3</sub>. Mg and Si concentrations were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian 720-ES. The reproducibility of the results was better than ±2.6% for Mg and ±3.0% for Si. PHREEQC (v.3. lnl-database) [17] was used to calculate saturation with respect to potential

secondary phases based on the measured fluid composition. Upon termination of the experiments, the reacted sepiolite samples were analyzed with XRD, SEM and energy dispersive X-ray spectroscopy (EDX). The experiment conducted at pH 7 (SEPD 7.0) was terminated after only 220 hours, due to persistent bacterial growth in the bottle and was therefore not considered further.

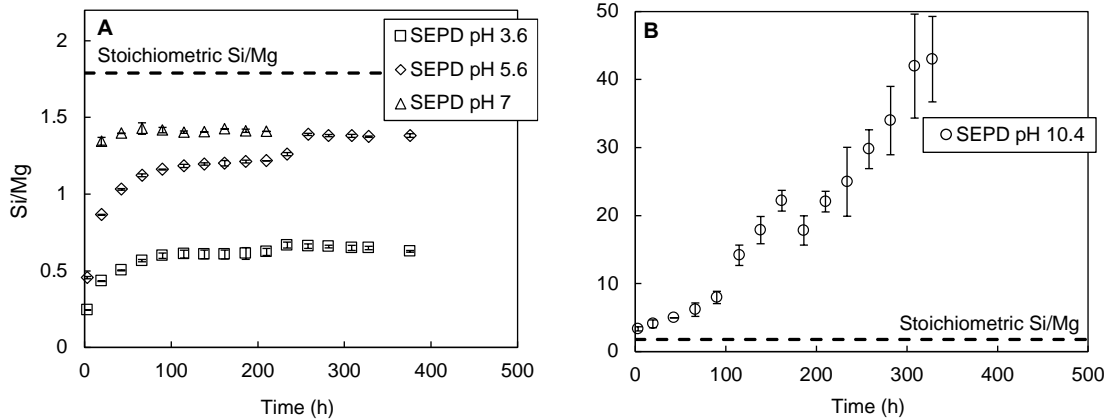


Fig. 1. Temporal change in the Si/Mg molar ratio in the fluid over time. Si/Mg ratio under acid and neutral conditions (A) and under alkaline conditions (B). The dashed line represents the atomic ratio of Si and Mg in the measured sepiolite. The error bars give the variation between the duplicate experiments. The errors are smaller than the symbols unless otherwise shown.

### 3. Results and Discussion

#### 3.1. Acidic conditions

Dissolution of sepiolite under acidic conditions (pH 3.6) was non-stoichiometric, as indicated by relatively constant and low aqueous Si/Mg ratios compared to sepiolite stoichiometry (Fig. 1). SEM-EDX analyses confirmed that the material remaining after termination of this experiment was comprised of only 0.854 at.% Mg, while the bulk of the solid was SiO<sub>2</sub> (Table 2). While Schott et al. [9] showed that the structure of wollastonite was preserved upon leaching of Ca, SEM imaging of the residual material in our experiments indicates that the crystal structure of sepiolite is not preserved (Fig. 2). This observation is confirmed by XRD measurements, which indicated that the reaction product is poorly crystalline, resembling amorphous SiO<sub>2</sub> (Fig. 3). PHREEQC calculations with the bulk solution chemistry suggest that the solution was undersaturated with respect to amorphous SiO<sub>2</sub> at the start of the experiment but reached supersaturation after approximately 200 hours, suggesting amorphous SiO<sub>2</sub> precipitation was feasible.

Although these results confirm the findings of previous studies, where divalent metals were found to be preferentially released from silicate-minerals [10,11,14,15,18,19], there is no consensus on the mechanisms by which Mg is preferentially released. It has been postulated that the release of Me<sup>2+</sup> in Me<sup>2+</sup>-silicates is driven by leaching from the interlayer [8,9], or by interface coupled dissolution-precipitation [13]. Alternatively, both mechanisms could contribute. The relative importance of leaching versus dissolution-precipitation in forsterite dissolution has been related to whether dissolution has reached steady state: at non-steady-state conditions leaching is favored, while at steady-state conditions dissolution-precipitation is the dominant dissolution mechanism [20]. The experimental results for sepiolite dissolution from this study are inconclusive as to whether leaching or dissolution-precipitation is dominant in the preferential release of Mg over Si under acidic conditions. The lack of any preservation of the original crystal structure upon dissolution could suggest that leached layers are not forming during sepiolite dissolution, yet if dissolution-precipitation mechanisms are at play, they are not tightly coupled to the interface as previously suggested for wollastonite [13]. However, a scenario in which amorphous SiO<sub>2</sub>(am) precipitates on the sepiolite surface is consistent with the available data. The aqueous Si concentration near the interface may be higher than in the bulk solution due to imperfect mixing, which may facilitate precipitation at the mineral surface prior to the bulk solution reaching amorphous SiO<sub>2</sub> saturation. Moreover, the sepiolite surface might decrease the energy

barrier needed to be overcome for  $\text{SiO}_2(\text{am})$  nucleation [21]. Although the surface could then facilitate  $\text{SiO}_2(\text{am})$  nucleation, the neo-formed precipitate did not maintain the surface morphology of the sepiolite (Fig. 2). Furthermore, precipitation of  $\text{SiO}_2(\text{am})$  upon sepiolite dissolution is consistent with the PHREEQC calculations that indicate supersaturation of  $\text{SiO}_2(\text{am})$ , implying that precipitation was possible. This could suggest that at least part of the reaction product is formed by dissolution-reprecipitation. The difference between the measured Si concentration and the calculated Si concentration assuming ideal stoichiometric dissolution with the measured fluid Mg concentrations suggests as much as 0.585 g of  $\text{SiO}_2(\text{am})$  could have been precipitated, if dissolution-reprecipitation were the mechanism of Si -enrichment. This would mean that over 50% of the 0.93 g of reaction product collected upon termination of the experiment consisted of  $\text{SiO}_2(\text{am})$ .

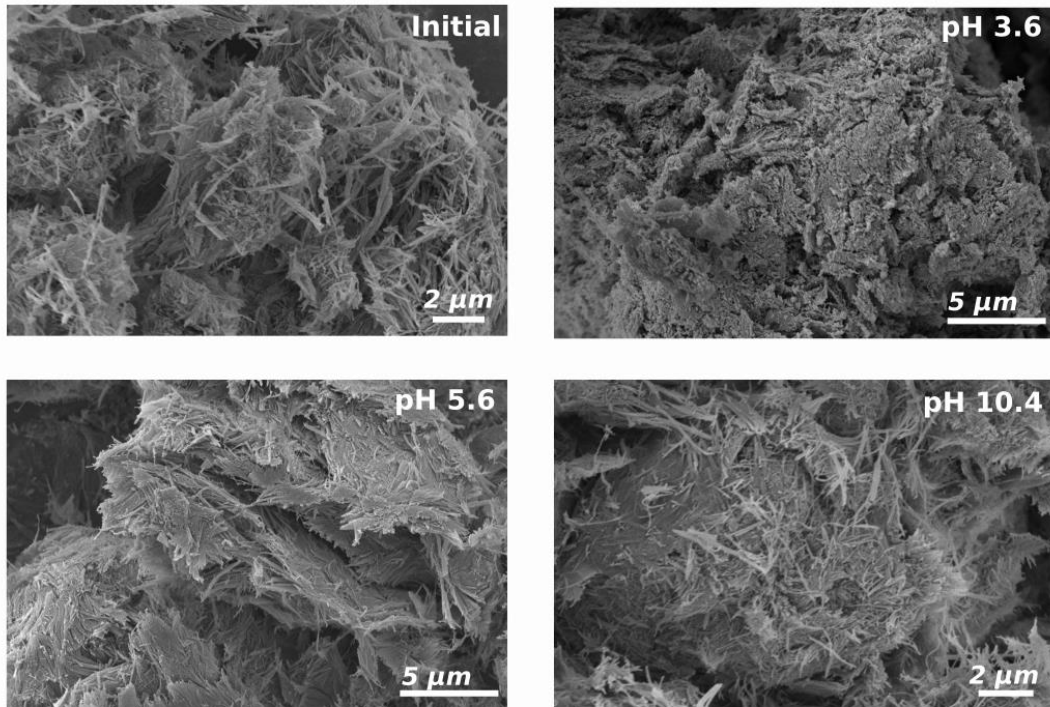


Fig. 2. Scanning electron micrographs of sepiolite. Notice that in the pH 3.6 experiment, the needle-like structure is not preserved and the reaction product appears to be an amorphous or poorly crystalline phase. In the pH 5.6 and pH 10.4 experiments the sepiolite structure is preserved and the solid are very similar to the pristine sepiolite.

Table 2. Semi-quantitative SEM-EDX results for three of the recovered reaction products and the initial sepiolite.

Sample	Si (at.%)	Mg (at.%)	O (at.%)	Si/Mg
SEPD pH 3.6	$34.8 \pm 0.85$	$0.854 \pm 0.094$	$64.5 \pm 0.52$	40.8
SEPD pH 5.6	$25.6 \pm 0.11$	$11.6 \pm 0.17$	$62.8 \pm 0.10$	2.21
SEPD pH 10.4	$24.3 \pm 0.040$	$13.5 \pm 0.064$	$62.2 \pm 0.017$	1.79
Initial Sepiolite	$24.7 \pm 0.43$	$12.9 \pm 0.66$	$62.4 \pm 0.23$	1.91

### 3.2. Mildly acidic and neutral solutions

Under mildly acidic (pH 5.6) and neutral (pH 7.0) conditions, dissolution was slightly non-stoichiometric, releasing more Mg relative to Si. The relative release rate of Si and Mg is found to remain constant over time at pH 7.0 but increases slightly with time at pH 5.6 (Fig. 1). Eventually, the Si/Mg ratio in SEPD 5.6 reaches the same ratio as in

the SEPD 7 experiment (Fig. 1). PHREEQC computations of the bulk solution composition show that  $\text{SiO}_2(\text{am})$  becomes supersaturated 375 hours into pH 5.6 experiment. The same procedure as described in section 3.1 is followed to calculate the amount of  $\text{SiO}_2(\text{am})$  potentially precipitated. This PHREEQC calculation reveals that 0.083 g of  $\text{SiO}_2(\text{am})$  could have been produced over the course of the pH 5.6 experiment, assuming that the non-stoichiometric dissolution of sepiolite could be solely attributed to precipitation of  $\text{SiO}_2(\text{am})$  and thus neglecting the “leached layer” mechanism. SEM-EDX analyses of the reaction product of SEPD 5.6 indicate that the relative amount of Mg and Si in the crystal structure has remained relatively constant during the experiment, although the reaction product is slightly enriched in  $\text{SiO}_2$  (Table 2). SEM images and XRD analysis confirm that there is no major change in the crystal morphology and structure between the initial sepiolite and the reaction product of SEPD 5.6 (Figs. 2, 3). Small changes in the XRD pattern can likely be attributed to changes in the sample preparation. There is no evidence for the precipitation of  $\text{SiO}_2(\text{am})$ .

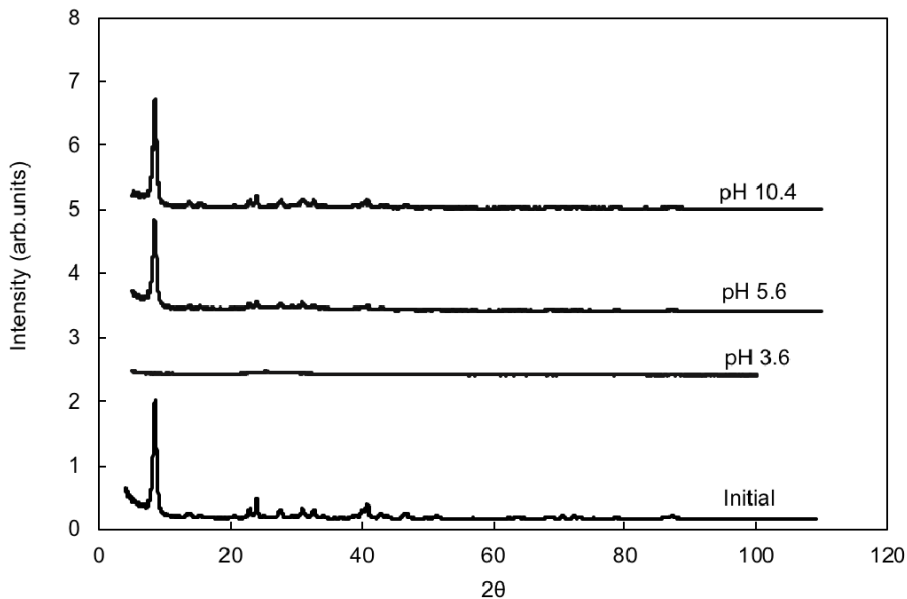


Fig. 3. XRD pattern obtained with Cu K ( $\alpha$ ) radiation. Notice that the spectrum from the pH 3.6 experiment does not show any peaks, while the XRD spectra for SEPD pH 5.6 and SEPD pH 10.4 roughly show the same peaks as the initial, pristine sepiolite. Small changes in the peak intensity of the initial sepiolite and SEPD pH 5.6 / SEPD pH 10.4 might be attributed to changes in the sample preparation for the XRD analysis.

The non-stoichiometric nature of sepiolite dissolution under mildly acidic and neutral pH conditions is inconsistent with the dissolution of other phyllosilicates, that tend to dissolve stoichiometrically [8,15,22]. Preferential release of Mg could be related to a structural effect, caused by the discontinuity of the octahedral sheets in the sepiolite structure. In continuous phyllosilicates, dissolution is limited by the detachment of the tetrahedral Si-sheet required to expose new  $\text{Mg}^{2+}$  octahedral sites. However, the channels within the sepiolite structure leave relatively more octahedral sites exposed, potentially facilitating  $\text{Mg}^{2+}$  release without the need to first dissolve the remaining Si-sheet. Preferential release of Mg from sepiolite, both at acidic and neutral conditions, facilitates  $\text{CO}_2$  sequestration by supplying the necessary divalent cations for carbonate mineral precipitation

### 3.3. Alkaline solution

Contrary to dissolution under acidic and neutral conditions, Si release was favored relative to Mg at pH 10.4 as indicated by Fig. 1. Over time the bulk solution became increasingly more depleted in Mg until after 350 h the Mg concentration fell below the detection limit of ~40 ppb. PHREEQC results indicate that no secondary phases were supersaturated, and XRD analyses and SEM images confirm that the reaction product is very similar to the initial

sepiolite (Figs. 2, 3). SEM-EDX analyses suggest that the reaction product has become more enriched in Mg compared to the initially added sepiolite (Table 2). Following a similar procedure as described in section 3.1., the saturation of Mg-rich phases that could have precipitated if Mg were released stoichiometrically was calculated using PHREEQC. These calculations indicated that brucite, commonly found to precipitate under ambient, alkaline conditions, was not supersaturated in the bulk solution. This does not exclude the possibility that secondary Mg-bearing phases may have been supersaturated at the sepiolite-fluid interface owing to inefficient mixing in the reactors.

The results for sepiolite dissolution under alkaline conditions are therefore inconclusive as to the mechanisms that drove preferential Si release. In forsterite the mineral structure facilitates the release of Si in alkaline solutions, but this not expected to occur for sepiolite dissolution under similar circumstances. In sepiolite the bond strength of Si in the tetrahedral sheet is speculated to be relatively high [23], making it harder to remove, whereas in forsterite, isolated SiO<sub>4</sub> tetrahedra are easily removed [14]. Concentrations of Mg near the mineral surface could have potentially been higher than measured in the bulk solution due to inadequate mixing. This may facilitate the precipitation of secondary phases such as brucite, commonly formed at high pH [24]. Although no evidence for precipitation of secondary phases was found using XRD analyses, SEM-EDX measurements do indicate that there is an increase in the relative amount of Mg over Si (Fig. 3, Table 2). Apart from Mg-rich mineral precipitation being favored at high pH, Kent & Kastner [25] found that under alkaline conditions Mg adsorbs onto both SiO<sub>2</sub>(am) and Mg-silicates. Adsorption of Mg on sepiolite upon initial release could potentially contribute to the relatively low Mg release in SEPD 10.4. However, these interpretations are very much speculative and require further investigation.

#### 4. Conclusions

Dissolution of sepiolite has been found to be non-stoichiometric under all considered conditions, preferentially releasing Mg under acidic and neutral conditions, while at alkaline pH Si is dominantly released. With these results alone, the dissolution mechanism cannot presently be deduced. However, this study indicates that under acidic conditions, given sufficient time, all Mg can be released from the crystal structure, leaving behind nothing but amorphous SiO<sub>2</sub>. Dissolution of sepiolite under acidic conditions thus provides ample divalent cations, necessary for CO<sub>2</sub> sequestration.

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