Release of Silicon and Aluminum from Montmorillonite Surfaces in Aqueous Systems

Ivan Sondi, Vlasta Tomašić, and Nada Filipović-Vinceković

Center for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia
Division of Physical Chemistry, Ruđer Bošković Institute, Zagreb, Croatia

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The release of silicon and aluminum from purified Na-montmorillonite surfaces in aqueous systems was investigated in dependence of pH at 25 °C. This study has shown that the dissolution of montmorillonite solid involves several parallel and sequential physico-chemical processes. The initial fast exchange of surface cations by hydrogen ions is followed by the release of aluminum and silicon. The dissolution rate of Si is higher than that of Al and influenced by the relative ratios of basal siloxane and edge surfaces. It is quantitatively described by the dissolution rate constants depending on pH. These results are in agreement with the heterogeneity of montmorillonite surfaces and the dominant presence of the siloxane basal surface. The shift of pH to more basic values by the ion exchange processes, and the hydrolysis of dissolved species, induces the formation of secondary amorphous solids, which may serve as precursors for the formation of amorphous aluminosilicates.

Keywords
aluminum
clay minerals
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montmorillonite
pH
silicon
surfaces

INTRODUCTION
Clay minerals are the main mineral constituents in rocks, sediments, and soils. They are a specific group of layer type hydrous aluminosilicate minerals, exhibiting physico-chemical characteristics of colloids, and belong to the general class of phyllosilicates. Due to their overwhelming diversity, their structural characteristics, and related unique surface chemical properties, clay minerals have commanded considerable interest in geo- and environmental sciences. Biogeochemical processes in soils and sediments are largely determined and governed by the mobility and reactivity of clay minerals as a result of their electrokinetic properties, large specific surface area, and high cation exchange capacity.

Smectites, the most common phyllosilicates in soils and sediments, are formed by weathering, diagenesis, or hydrothermal processes which can either involve degradation and transformation of mineral precursor phases, or precipitation from solution. Dissolution and precipitation processes of smectite clays are important in the formation and diagenesis of soils and sediments, and in global cycling of elements. Furthermore, these processes are important for numerous industrial applications, waste water treatment, and long-term behaviour of man-made barriers used in deposition of contaminants.

Literature abounds with studies of dissolution processes of aluminosilicate minerals and of a variety of clay minerals, including smectites. In the last decade

* Author to whom correspondence should be addressed. (E-mail: sondi@irb.hr)
studies investigating the kinetics of dissolution processes of smectite clay minerals were reported, mostly in highly acidic\textsuperscript{17,18} or highly basic solutions,\textsuperscript{19} but rarely, if any, in neutral aqueous media. Zysse and Schindler\textsuperscript{18} have studied the proton promoted dissolution kinetics of K-montmorillonite in HCl/KCl solutions at pH = 1 to 5 at constant temperature of 25 °C. They have shown that the dissolution rate for Si and Al increased with concentration of KCl and decreased with increasing pH. The combined effect on the smectite dissolution rate at pH = 1 to 4 and temperature from 25 to 70 °C, was reported by Amram and Ganor.\textsuperscript{17} It was shown that the dissolution rate increases with temperature and decreases with pH. Cama and coworkers\textsuperscript{19} studied dissolution kinetics at elevated temperature under basic conditions (pH = 8.8). They found that the dissolution rate of smectite decreases as a function of the Si concentration, while is not inhibited by the presence of Al.

Recently, a number of dissolution studies on phyllosilicates were reported by using atomic force microscopy (AFM) under either alkaline or acidic conditions.\textsuperscript{20,21} In comparison with classical batch-experiments, these studies enable in-situ observation of dissolving clay particles at the molecular scale, particularly the anisotropic dissolution of their most reactive surface sites. These are distributed unevenly between the basal planes, and edge faces \{110, 010\}. In general, it was found that dissolution is much faster on edge surfaces than on basal planes.

There are many examples of inconsistencies, and a wide spread in measured dissolution rates within the same class of clay minerals. Two factors influence these inconsistencies. The first pertains to the method of preparation and surface purification of the clay samples prior to the dissolution experiments;\textsuperscript{19} the second to the weathering history and mechanical wear of the source clay particles, which governs the ratio between basal siloxane and edge surfaces.\textsuperscript{22}

This study aims to study the dissolution process, particularly the release of silicon and aluminum, from natural, purified, and well-defined smectitic Na-montmorillonite particles in aqueous media over broad pH range from 0.9 and 9. It assess the degree to which short-term laboratory experiments are significant for studies of natural dissolution processes in aqueous media under acidic, neutral, and basic conditions. In addition the formation of a secondary solid phase from the initially dissolved species is described. It contributes to the understanding of the mechanisms of dissolution of aluminosilicate clays (smectites) in sediments and soils, and subsequent early diagenetic formation of secondary colloidal solids lacking a crystalline structure.

**MATERIALS AND METHODS**

**Materials**

All experiments reported in the present study were performed on purified natural montmorillonite extracted from bentonite from the Ivanić Grad region in northern Croatia. The chemical and mineralogical characteristics of this sample were determined by Braun.\textsuperscript{23}

In order to extract a pure fraction of montmorillonite from a natural clay sample, and to remove organic and inorganic impurities from the mineral surface the following experimental procedures were used. First, the sample of bentonite clay was dispersed in deionized water in order to remove soluble salts and grit. The suspension was left in water for a week and then the fraction of the size of < 2 μm was separated by centrifugation. The small amount of calcite from the separated fraction was removed by treatment with sodium acetate–acetic acid.\textsuperscript{24} The sample was then treated with diluted Na-acetate buffered H₂O₂ to remove organic matter, and then with a citrate-bicarbonate-dithionate solution to remove crystalline and amorphous iron oxides and oxyhydroxides.\textsuperscript{25} Next, the sample was again suspended in deionized water, washed several times, and finally, a clay mineral fraction of the size of < 1 μm was obtained from this dispersion by centrifugation. The monoionic Na-form of montmorillonite was prepared by ion exchange, following the method of Karen and Shainberg.\textsuperscript{26} Finally, the clay mineral suspension was dialyzed in deionized water, and obtained as a dried powder by freeze drying and kept for future experiments.

The specific surface area (SSA) and the cation exchange capacity (CEC) of the prepared Na-montmorillonite sample were determined to be 78 m² g⁻¹ and 117 meq/100 g, respectively. The X-ray diffraction pattern of oriented sample showed that the extracted fraction consists of almost pure montmorillonite (Figure 1) Measurements of electrophoretic mobility of this sample, suspended in a single electrolyte solution of 1 × 10⁻³ mol dm⁻³ NaCl, as a function of pH, indicated electrophoretic properties typical of smectite minerals\textsuperscript{27} and absence of surface impurities\textsuperscript{27} (Figure 2).

*Figure 1. XRD pattern of (a) source bentonite sample and (b) separated and purified montmorillonite analysed as oriented sample. The diffraction peaks on the XRD patterns were coded as follows: Mo-montmorillonite, I-illite, Ca-calcite, F-feldspars, Cr- cristoballite.*
Methods

Mineral composition of the bentonite clay, the efficiency of separation, and the final structural properties and purity of montmorillonite were determined by a Philips 1070 PW X-ray diffractometer. The specific surface area (SSA) of clay particles was determined by single point nitrogen adsorption, using a Micromeritics FlowSorb II 2300 instrument. The cation exchange capacity (CEC) was determined using ammonia exchange and an ammonia selective electrode. The measurements of pH were performed by a combined electrode connected to an ion analyzer (Orion Research, Model 901). Electrokinetic measurements of clay mineral particles were made using a PenKem S3000 instrument.

The dissolution of montmorillonite was performed in batch reactors at 25 °C where 1 gram of dry Na-montmorillonite solid was suspended in 100 ml of deionized water of adjusted initial pH in batch reactors. The pH of solutions was adjusted by addition of HCl or NaOH. The dispersions were equilibrated for 5 minutes under gentle magnetic stirring at 25 ± 0.1 °C. All experimental systems were prepared in triplicate. The concentration of released silicon and aluminum were measured in intervals of days over time periods of up to 50 days. The solutions were analyzed after clay solids were removed by centrifugation of the suspension at pre-determined time intervals. The concentrations of silicon and aluminum in the residual solution were determined by inductively coupled plasma atomic emission spectrometry (ARL 35000 C-ICP emission spectrometer equipped with argon ICP). The Al/Si molar ratio in the amorphous gel phase was estimated from the decrease of Al and Si concentration in suspensions prepared at pH = 9, for reaction times between 1 and 7 days. The assumption was that the entire loss of Si and Al from the solution phase, is appearing in the gel phase, and retains the same Al/Si ratio.

RESULTS

The changes of pH with time for the Na-montmorillonite suspensions at different initial pH (pHi) values of aqueous solutions for a short (up to 5 minutes) and prolonged reaction time (up to 50 days) are displayed in Figure 3 a,b. The initial rapid change of pH during the first 5 minutes of reaction is mostly attributed to the protonation of the edge surface sites and cation exchange reaction between H+ and Na+. The extent, to which the hydrogen ions from aqueous phase protonate the edge surface and governs cation exchange reaction, depends on pHi of solutions. The process of protonation and cation exchange reaction was wound up within a five minutes. At pHi of 0.9 and 1.5, when the H+ concentration was high, only small changes in pH were nevertheless observed. At the pHi = 2.0 and 2.5, an increase in pH of the solution was instantly observed. Subsequently, these systems showed a gradual increase (pHi = 2.0) or almost a constant value (pHi = 2.5) with time. If the pHi of the systems was > 3.0, a rapid pH shift to a high pH was observed followed by a gradual decrease with time.

The release of aluminum into the bulk solution as a function of time and pHi is given in Figure 4. In the acid region (pH = 0.9 and 1.5) the aluminum concentration in solution increased in the measured period. Due to the high acidity, released aluminum exists in solution as...
Al(H$_2$O)$_6$$_3^+$ or (AlOH(H$_2$O)$_5$)$_2^+$. If the hydrogen ion concentration was close to, or equal to the amount of exchangeable cations, the aluminum concentration rapidly reached a steady-state value, and then, after two days, declined to less than 3 $\times$ 10$^{-6}$ mol dm$^{-3}$ at pHi = 2.0, whereas at pH = 2.5 small and constant concentration of dissolved Al was measured thorough the whole time of experiments. When the initial pH was higher (3, 6, 4, and 9) the time dependent aluminum concentration first increased and then decreased. According to the literature, at pH > 7 Al(OH)$_4^-$ is the predominant Al species in solution.

The release of silicon, as a function of the pH$_i$ and time, is shown in Figure 5. The trends of the curves are similar to those obtained for aluminium, but the concentration of dissolved silicon was always greater than that of dissolved aluminium. At pH < 9, released silicon is present in the form of monomeric acid, H$_3$SiOOH$_3$, while at pH above 9, the dominant species in solution are H$_3$SiO$_4^-$ and H$_3$SiO$_4^{2-}$.

After aging the montmorillonite solid for $t > 2$ days in solutions with pH$_i \geq 3$, the decrease of pH, and both, Al and Si concentrations, indicated that dissolution processes are followed by precipitation. The secondary solid phase appeared as an amorphous gel phase. The Al/Si molar ratio in the amorphous gel phase (Al/Si = 0.8) was slightly higher than in the solid montmorillonite (Al/Si = 0.45).

**DISCUSSION**

There are several processes that should be addressed in order to interpret the obtained results. The first refers to the initial changes of pH caused by protonation of edge surface of montmorillonite and the ion exchange reaction between hydrogen ions and exchangeable cations (Figure 3a,b). This process was completed within a few minutes, and during this short period, a negligible amount of silicon and aluminum was released into the solution. What followed was a slow pH change during the aging process, and the release of Si and Al into the solution. In order to show the preferential release or retention of Al with respect to Si the relative molar ratios, RRR, were calculated. The RRR is the molar ratio of aluminium and silicon in the aqueous solution (Al/Si)$_{aq}$ normalized to the ratio in the unaltered solid phase (Al/Si)$_{solid}$ Eq. (1).

$$RRR = \frac{(Al/Si)_{aq}}{(Al/Si)_{solid}} \tag{1}$$

Thus, in the case of congruent release, (RRR) = 1. In contrast, two cases are distinguished for incongruent dissolution: (i) preferential release of Al (RRR > 1) as a consequence of dAl/dt > dSi/dt, and/or (ii) preferential retention of Al (RRR < 1) as a result of dAl/dt < dSi/dt.

The RRR values for various initial pH values are shown in Figure 6. The values were lower than 1 for almost the entire experimental range. Initially, Si was preferentially released from the montmorillonite structure with respect to Al. Al was preferentially released...
The dependence of $k$ is the exponent which implies a fractional rate order. The RRR decrease was also observed at initial pH = 2.0 and 2.5, although it was becoming less pronounced at pH = 2.5. The suspensions prepared at initial pH = 3 and 6.4 showed relatively constant RRR values up to 7 days. Later on, the RRR values decreased significantly. Changes in RRR values (Figure 6) as well as pH (Figure 3b) with time indicated that for $t > 1$ day the concentration change of Si and Al in the bulk phase might be ascribed to other processes, i.e. to the dissolution followed by hydrolysis of dissolved species and secondary precipitation.

The change of silicon and aluminium concentration, $C$, with time for $t < 2$ days obey the empirical relation:

$$C = k \cdot t^n$$

where $t$ is the aging time in days, $k$ is the constant and $n$ is the exponent which implies a fractional rate order. The dependence of $k$ and $n$ on the pH, attained after 5 minutes of preparation are given in Table I. The $k$ tends to decrease with increasing pH for both Al and Si. The decrease continues until the concentration of hydrogen reaches a value corresponding to the amount of exchangeable cations ($2 > \text{pH}_i < 3$). In this region $k_{Si}$ reaches minimum value and attained a steady state. After that point, the rate constant increases to values higher than before. The constant of silicon dissolution was significantly lower than that for aluminium in acidic to weakly alkaline solution. This is consistent with results of Golubev and co-workers who reported the dissolution ratio of Al/Si significantly lower than that for the source solid phase. They attributed this to the re-adsorption of dissolved Al on the interlayer sites.

The dissolution rate of 2:1 sheet aluminosilicate structures is difficult to interpret: their surface is anisotropic and characterized by structurally dependent distribution of reactive sites over it. Numerous studies have shown that hydroxide oxide groups at edge surfaces of phyllosilicates represent major reactive sites, and dissolve at faster rates than basal siloxane surfaces. The area of edge surfaces varies depending on the type of the clay minerals, whereas for smectite clay minerals it is less than 1 %. In addition the fraction of edge surface of clay mineral particles depends on the degree of physical disintegration. Therefore, it is difficult to compare the dissolution rate of the same type of clay minerals of different sources. Na-montmorillonite used in this study contains only a small percentage of reactive edge surfaces which is indicated by electrophoretic mobility data and the absence of a measurable isoelectric point (Figure 2). Higher dissolution rates of Si vs. Al imply the possibility of Si release during the dissolution process from chemically less reactive, but preponderant basal siloxane surfaces. From the other side, the same empirical rate law found for Si and Al (Eq. (1)) indicated a congruent dissolution. Accordingly, it seems that contribution of Si from basal planes (consisting only of siloxane layers) and partial re-adsorption of dissolved Al by ion exchange or by surface complexation. These mechanisms resulted in higher concentration of Si over Al in solution.

Aluminosilicate dissolution experiments have led to various interpretations about the rate-determining steps. Generally, the linear and logarithmic rate laws ($n = 0$, and $n = 1$) result from the rate-determining surface processes, while parabolic dependences ($n = 0.5$) result from a diffusion controlled dissolution processes. Dibble and Tiller have shown that many surface rate processes can be dominated by diffusion. For example, parabolic time dependence results if the kink spacing increases as a function of time $t^{1/2}$ owing to kink poisoning reactions controlled by diffusion; diffusion of a reaction product or impurity ion to or from the interface could become a rate-determining step if adsorption retards kink or layer motion; diffusion dominates the reaction of surface reconstruction. It can be seen from the Table I that surface processes are the rate determining processes for suspensions prepared at initial pH = 2.0 and 2.5. The $n$ obtained in other experiments indicates that several processes occur simultaneously. There is no indication in other experiments of an unequivocal answer of either surface or diffusion control.

After $t > 1$ days suspensions prepared at initial pH > 3 displayed a decrease of Al and Si concentrations because of precipitation. Bulk precipitation of Si and Al can occur under appropriate conditions of pH and concentration. The maximum concentration of Al and Si in the solution (Figures 4 and 5) are in good agreement with the solubility of amorphous Al(OH)$_3$ and amorphous SiO$_2$ and uphold the hypothesis of secondary precipitation of these phases.

<table>
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<th>pH$_i$</th>
<th>pH$_{5\text{min}}$</th>
<th>log $k$</th>
<th>log $n$</th>
<th>log $k$</th>
<th>log $n$</th>
</tr>
</thead>
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<tr>
<td>0.9</td>
<td>0.85</td>
<td>-3.57</td>
<td>0.20</td>
<td>-3.00</td>
<td>0.40</td>
</tr>
<tr>
<td>1.5</td>
<td>1.56</td>
<td>-3.79</td>
<td>0.19</td>
<td>-3.09</td>
<td>0.40</td>
</tr>
<tr>
<td>2.0</td>
<td>5.99</td>
<td>-4.76</td>
<td>0.02</td>
<td>-3.76</td>
<td>0.25</td>
</tr>
<tr>
<td>2.5</td>
<td>8.50</td>
<td>-5.52</td>
<td>0</td>
<td>-3.75</td>
<td>0.20</td>
</tr>
<tr>
<td>3.0</td>
<td>10.40</td>
<td>-2.79</td>
<td>0.38</td>
<td>-2.32</td>
<td>0.17</td>
</tr>
<tr>
<td>6.4</td>
<td>10.50</td>
<td>-2.52</td>
<td>0.47</td>
<td>-2.34</td>
<td>0.17</td>
</tr>
</tbody>
</table>
Both the tendency of hydrosilicates to organize with time towards a clay mineral structure and the presence of the amorphous aluminium hydroxide Al(OH)$_3$ promote the formation of amorphous aluminosilicate. The decrease in pH, observed after the onset of secondary phase formation, indicates reorganization of the amorphous phase toward aluminosilicate with molar Al/Si ratio characteristic for the smectite group.

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Minerali glina predstavljaju grupu hidratiziranih alumosilikata koja je široko zastupljena u sedimentima i tlu. Smektiti (montmorilonit) se pojavljuju samo u najsitnijim frakcijama i imaju značajnu ulogu u biogeokemijskom kruženju tvari u okolišu. Jedan od osnovnih fizikalno-kemijskih procesa na površinama glina u vodenim sustavima je otapanje i otpuštanje njihovih strukturnih elmenata, prvenstveno siličija i aluminija. U radu je istraživano otpuštanje siličija i aluminija s površine prirodnog montmorillonita u vodenim otopinama pri pH vrijednostima od 0,9 do 9 i konstantnom temperaturom od 25 °C. Iz ekperimentalnih podataka izračunata je i konstanta brzine otapanja za siličij i aluminiu u vremenskom periodu manjem od 2 dana. Utvrđeno je, da je brzina otapanja za siličij veća nego za aluminiu i posljedica je veće zastupljenosti siloksanske površine u ukupnoj površini montmorillonita.