

# Dissolution of phyllosilicates under saline acidic conditions

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## Abstract

The effect of saline acidic conditions on the dissolution rates of kaolinite, illite and montmorillonite was investigated. The dissolution experiments were carried out at pH 1 and 2 at 25°C under far from equilibrium conditions using stirred flow-through reactors. The dissolution rates were calculated on the basis of steady state Al and Si concentrations, except for illite dissolution experiment at pH 2, where the rate was calculated from Al release rate. There is a good agreement between the estimates obtained from Al and Si values for the dissolution rates of studied minerals. An initial rapid and incongruent release of elements was followed by a slow and congruent release rate at the steady state. Preferential release of Al at the initial stages was observed for kaolinite and illite in all the experiments while no such trend was observed for smectite. The calculated (log Al) dissolution rates at pH 1.0 and 2.06 are -12.61 and -13.30 for kaolinite, -12.79 and -12.86 for illite and -12.64 and -12.92 for smectite, respectively. Our results showed higher dissolution rates of kaolinite under saline acidic conditions as compared to the non-saline acidic conditions.

## Key Words

Steady state, acidity, clay minerals, pyrite, acid sulfate soils, aluminosilicates.

## Introduction

Pyrite is the most commonly occurring iron sulfide mineral in soils and it forms in anaerobic soil materials. Oxidation of pyrite due to natural and anthropogenic activities leads to the release of copious amounts of sulfuric acid in soil and water environments, and formation of acid sulfate soils (ASS). In Australia, many different types of ASS have been found because of diversified hydrology and biogeochemistry in different areas of the continent. The two main types include coastal and inland ASS. Coastal ASS cover an area of 95,000 km<sup>2</sup> in Australia. Most of these soils lie beneath coastal estuaries and tidal basins and many are very close to significantly populated centres. Inland ASS were not given much attention until the identification of sulfidic sediments in inland non-tidal seepage area of Mt. Lofty Ranges, South Australia (Fitzpatrick *et al.* 1996), wetlands of Murray Darling Basin (Lamontagne *et al.* 2004) and the sediments of Bottle Bend Lagoon (McCarthy *et al.* 2006).

A soil becomes acidic when acid neutralizing processes in the soil consume less H<sup>+</sup> than is being produced by the acid producing processes. The components of the soil with a capacity to neutralize acidity generated by various processes include soil solution, exchange complex and minerals. Mineral dissolution becomes the major acid consuming process in highly acidic systems with pH ≤ 4. Phyllosilicates in soils have the largest capacity to consume acidity generated by various processes because of their presence in soil in large quantities. Although the dissolution of phyllosilicates occurs over the whole pH range, the rate of dissolution increases as the pH decreases in the acidic pH range (Rozalen *et al.* 2008). The acid neutralization from phyllosilicates dissolution is strongly dependent on their respective dissolution rates. In the past few decades many studies were conducted to determine the dissolution rates of kaolinite (Cama and Ganor 2006; Cama *et al.* 2002; Huertas *et al.* 1999; Nagy *et al.* 1991; Yang and Steefel 2008) while only a few studies have measured dissolution of illite (Kohler *et al.* 2003) and montmorillonite (Amram and Ganor 2005; Golubev *et al.* 2006; Huertas *et al.* 2001; Rozalen *et al.* 2008) under different solution conditions. These past studies were conducted under different temperatures and input solution compositions, however, none of them measured the dissolution of phyllosilicates in saline acidic environments. The aims of the present study were to determine the dissolution rates of most commonly occurring phyllosilicates in Australia, i.e. kaolinite, illite and montmorillonite, in saline acidic input solutions, and to determine the effects of pH and ionic strength on mineral dissolution rates.

## Methods

### Pre-treatment and characterization

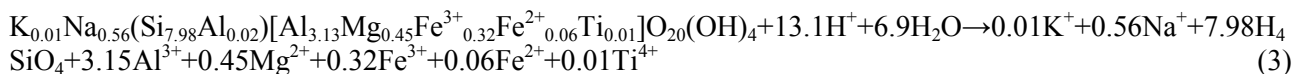
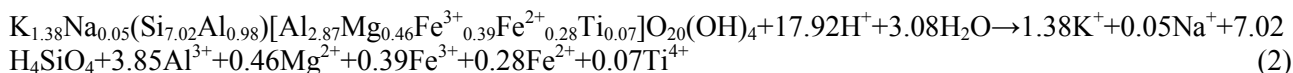
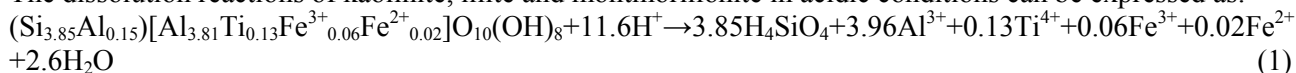
Kaolinite (KGa-2), illite (IMt-2) and montmorillonite (SWy-2) samples were obtained from the Source Clay Repository of the Clay Minerals Society. After separating the clay fraction (<2 µm), the mineral samples were saturated with Na<sup>+</sup> and washed repeatedly to remove excess salts before freeze drying. Mineralogical characterization of the pre-treated samples was done by X-ray diffraction (XRD). Minor amounts of quartz were found in both montmorillonite and illite samples, and rutile was observed in kaolinite. The bulk chemical composition of the clay samples was determined using X-ray fluorescence (XRF) and Fe(II) in the mineral samples was determined by the 1, 10 phenanthroline method (Amonette and Templeton 1998). The structural formulae of minerals was calculated from the XRF and Fe(II) data (Cicel and Komadel 1994). The corresponding Al/Si ratios obtained from structural formulae of kaolinite, illite and montmorillonite are 1.03, 0.55 and 0.40, respectively. The specific surface area of the Na-saturated clay samples was measured by five point N<sub>2</sub> adsorption using Brunauer-Emmett-Teller method, and the values were 21, 42 and 37 m<sup>2</sup>/g for kaolinite, illite and montmorillonite, respectively.

### Experimental settings

Dissolution experiments were carried out using stirred flow-through reactors (46 mL volume). The experiments were conducted at 25±1°C by immersing the reactors in a thermostatic water bath held at the desired temperature. A constant flow rate of the input solution was maintained by a Gilson peristaltic pump. Flow rate range of 0.02-0.05 mL/min was used in different experiments. The flow rate and input solution composition were kept constant for long enough time to reach the steady state. The input solutions at specific pH were prepared by diluting concentrated H<sub>2</sub>SO<sub>4</sub> with E-pure water and NaCl was used to maintain a constant ionic strength of the solution. The effluent solution was collected every day and the total concentrations of Al and Si were determined colorimetrically by Catechol violet (Dougan and Wilson 1974) and Molybdate blue method (Koroleff 1976), respectively. The concentrations of Ca, Fe, K, Mg and Na were determined by inductively coupled plasma atomic emission spectroscopy. The variations in the output Al and Si concentrations and pH were monitored throughout the duration of each experiment while the amounts of Fe, K, Mg and Na were determined for only selected samples when steady state was reached for Al and Si. The experimental conditions for all experiments and the concentrations of Al and Si at steady state are presented in Table 1.

### Kinetics calculations

The dissolution reactions of kaolinite, illite and montmorillonite in acidic conditions can be expressed as:



The equilibrium constants for the dissolution reactions of illite and montmorillonite were computed from equations and parameters reported by Vieillard (2000). For kaolinite dissolution reaction a log  $K_{\text{eq}}$  value of 8.95 reported in earlier studies (Nagy *et al.* 1991) was used.

The dissolution rate (mol/m<sup>2</sup>s) in a stirred flow-through reactor was calculated from the release rate of Al or Si at the steady state by using the following equation (Cama *et al.* 2000):

$$\text{Rate}_j = -\frac{1}{V_j} \frac{q}{SM} (C_j) \quad (4)$$

where  $C_j$  is the concentration of component  $j$  (Al or Si) in the output solution (mole/L),  $q$  is the fluid volume flow through the reactor (L/s),  $S$  is the specific surface area (m<sup>2</sup>),  $M$  represents the mineral mass (g) and  $V_j$  is the stoichiometric coefficient of component  $j$  in the dissolution reaction.

The saturation state of the solution with respect to mineral (kaolinite, illite or montmorillonite) dissolution was calculated in terms of Gibbs free energy of reaction  $\Delta G_r$ :

$$\Delta G_r = RT \ln \left( \frac{\text{IAP}}{K_{\text{eq}}} \right) \quad (5)$$

where IAP is the ion activity product,  $K_{eq}$  is the equilibrium constant, T represents the absolute temperature and R is the gas constant. Activities of various ions in the solution were calculated using *Visual MINTEQ* V 2.61 geochemical model.

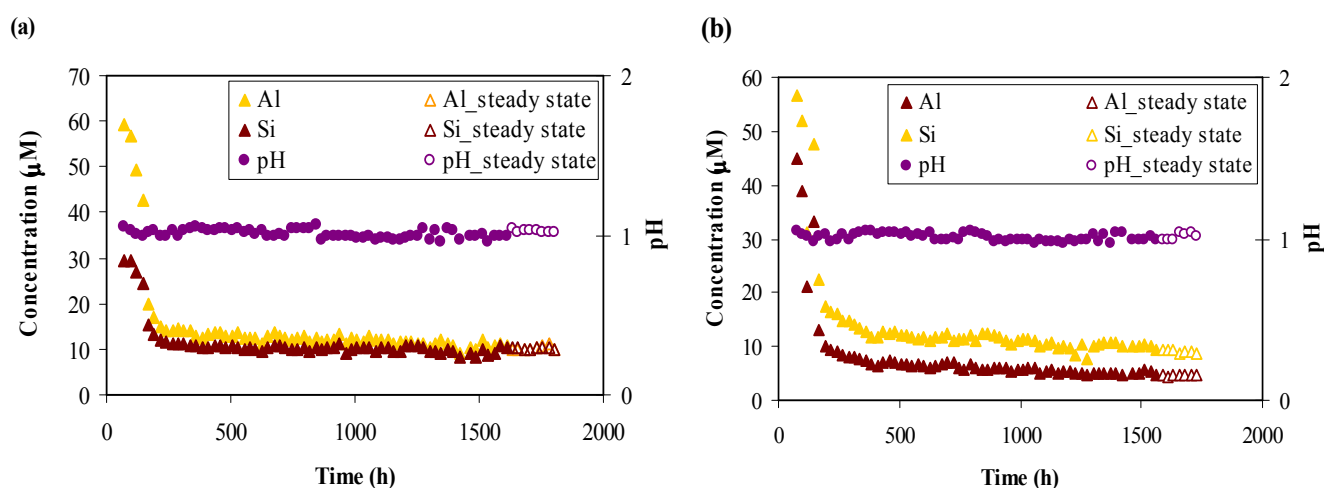
## Results

The dissolution was very fast at the start of each experiment with rapid, incongruent release of Al, and Si which became slower after first 200 hours of the experiment as shown in Figure 1. In kaolinite and illite experiments, initially Al was released at a much faster rate than Si and continuously decreased before reaching the steady state. In case of montmorillonite dissolution, there was not much difference in the initial release rate of Al and Si. The steady state concentrations of Al and Si for kaolinite and illite showed a congruent dissolution of these minerals at the studied experimental conditions while a higher Al release was observed for montmorillonite under saline acidic conditions.

**Table 1. Dissolution rates for kaolinite, illite and montmorillonite at pH 1 and 2 in 0.25 M NaCl solution at 25°C**

Mineral	Initial mass (g)	pH input	Flow rate (mL/min)	Duration (h)	C Si out ( $\mu\text{mol/L}$ )	C Al out ( $\mu\text{mol/L}$ )	Al/Si	log Rate Si ( $\text{mol/m}^2\text{s}$ )	log Rate Al ( $\text{mol/m}^2\text{s}$ )
KGa-2	0.4014	1.00	0.0477	1803	10.1	10.2	1.01	-12.61	-12.61
KGa-2	0.3885	2.06	0.0377	2170	2.63	2.62	1.00	-13.28	-13.3
IMt-2	0.1163	1.00	0.0431	1890	8.48	4.16	0.49	-12.75	-12.79
IMt-2	0.1164	2.06	0.0545	1677	3.1	2.84	0.96	-	-12.86
SWy-2	0.1221	1.00	0.0428	1731	9.11	4.61	0.51	-12.74	-12.64
SWy-2	0.1226	2.06	0.0357	1942	5.47	2.87	0.52	-13.05	-12.92

Our results for kaolinite dissolution experiment at pH 1 and 2 and 0.25 ionic strength showed a significant increase in the mineral dissolution rate (Table 1) as compared to the previous studies conducted at lower ionic strengths. Cama *et al.* (2002) reported a dissolution rate of -12.96 and -13.47 for kaolinite (KGa-2) at pH 1 and 2 and ionic strength of 0.12 and 0.011, respectively. Zysset and Schindler (1996) also reported a higher dissolution rate for K-montmorillonite in 1 and 0.1 M KCl solutions than in 0.03 M KCl solution. To evaluate the effect of ionic strength on the dissolution of illite and montmorillonite, we are conducting further experiments.



**Figure 1. Variation in Al and Si concentrations and pH as a function of time in two representative flow-through dissolution experiments conducted at pH 1.0 (a) kaolinite and (b) smectite**

## Conclusion

The preliminary results suggest that the effect of pH on the dissolution rates of the kaolinite, illite and montmorillonite is similar, indicating a common rate limiting step in the dissolution of phyllosilicates. The dissolution rate of kaolinite appears to have increased with increasing ionic strength of the solution. However, further experiments are needed to confirm these results for all three minerals.

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