

Dissolution of clay sediments in acid-sulfate systems

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Introduction

Significant quantities of sulfidic sediments have been reported to have recently accumulated in inland wetlands of Murray Darling Basin due to a combination of long periods of inundation and the entrance of sulfate-rich water (Fitzpatrick and Shand, 2008). Sulfidic sediments have a capacity to produce copious amount of acidity on exposure to aerobic conditions (Fitzpatrick and Shand, 2008). These processes will cause soil acidification if the buffering capacity of soil is less than the amount of acidity produced. The dissolution of phyllosilicate minerals may occur if soil pH decreased below 4 in acid sulfate soils (ASS). The quantification of the mineral dissolution rates in ASS is imperative to understand the mechanism and parameters controlling the acid neutralization processes and their impact on the soil environment. The aim of this study was to investigate the dissolution behaviour of the clay material from an inland ASS in solutions with the composition similar to inland ASS.

Materials and Methods

The clay sample used in the dissolution experiments was separated from a soil core collected from an inland wetland, Bottle Bend lagoon near Mildura in NSW. The < 2 µm fraction of the sample separated by sedimentation-resuspension procedure and was saturated with Na. Specific surface area of the Na-saturated clay sample was determined by five point N₂ Brunauer-Emmett-Teller method. Chemical composition of the clay sample was determined by X-ray fluorescence spectroscopy (Norrish and Hutton, 1977) and Fe(II) was analysed by 1, 10 phenanthroline colorimetric method (Amonette and Templeton, 1998). The minerals present in the clay sample were identified using X-ray diffraction (XRD) patterns of both randomly and basally oriented specimens. The quantitative analysis of the clay sample was done by Mark Raven (CSIRO, Adelaide) using random powder XRD data of the Ca saturated clay using SIROQUANT (Taylor, 1991).

Clay dissolution experiments were performed using the experimental set-up as described by Bibi et al. (2011b). The dissolution experiments were conducted in flow-through reactors immersed in thermostatic water baths at 25°, 35° and 45°C. Input solution consisted of diluted H₂SO₄ at pH ranging from 1 to 4 and at two ionic strengths of 0.01 and 0.25 M (NaCl). A fixed Sample mass (0.1 g) was placed into the reaction chamber of the flow-through reactors and the experimental conditions in each experiment were kept constant until the steady state was achieved. The output solution was collected every 24 h and the concentrations of Si and Al were analysed using colorimetric analytical

methods (Dougan and Wilson, 1974; Koroleff, 1976). The output solution concentrations of K, Fe and Mg were determined by ICP-AES in each sample.

Dissolution rate of the clay sample was calculated from the steady state concentrations of Si, Al and Fe using the following expression (Cama et al., 2000):

$$R_j = \frac{F}{SM}(C_j) \quad (2)$$

where, C_j is the steady state concentration of Si, Al or Fe in mol/L, M is the initial sample mass (g), S is the specific surface area (m²/g) and F (L/s) is the fluid flow rate.

Under acidic conditions, the pH dependence of the dissolution rate of clay can be described by the rate law expression as (Nagy, 1995):

$$R = k[H^+]^n \quad (3)$$

where R is the clay dissolution rate (mol m⁻²s⁻¹), k is the reaction constant, $[H^+]$ is the activity of protons and n is the reaction order; plotting $\log R$ vs. pH allows the reaction order- n to be determined.

The temperature dependence of clay dissolution rate at constant pH was described by using the Arrhenius equation (Nagy, 1995):

$$R = A \exp\left(\frac{-E_{app}}{RT}\right) \quad (4)$$

where A (mol cm⁻²s⁻¹) is the pre-exponential factor also known as the frequency factor, E_{app} (kcal mol⁻¹) is the apparent activation energy, R is the gas constant and T is the absolute temperature (K).

Geochemical speciation calculations of the output steady state solutions were performed using the geochemical speciation program PHREEQC (Parkhurst and Appelo, 1999).

Results and Discussion

The quantitative XRD analysis of the clay showed the dominance of montmorillonite (62%) in the sample with nearly equal proportion of illite (18%) and kaolinite (15%).

The release rate of Si and Al was much faster initially which decreased with time and steady state concentrations were observed after 570 to 2015 h depending on the solution pH and temperature. The initial fast release of ions (Fig. 1) could be attributed to several factors including the depletion of ultra-fine particles and a reduced availability of highly reactive sites on the mineral surface (White and Brantley, 2003). An exception to the trend mentioned above was observed for Al release in pH 3 and 4 experiments at the lower ionic strength of the solution and this may have resulted from the

adsorption of dissolved Al on the mineral surfaces (Bibi et al., 2011b). Stoichiometry of the clay dissolution reaction was assessed from a comparison of the elemental ratios (Al/Si, K/Si, Fe/Si and Mg/Si) in the output solution to their ratios in the original clay sample. The Al/Si, K/Si, Fe/Si and Mg/Si ratios of the original clay sample were 0.57, 0.06, 0.13 and 0.03, respectively.

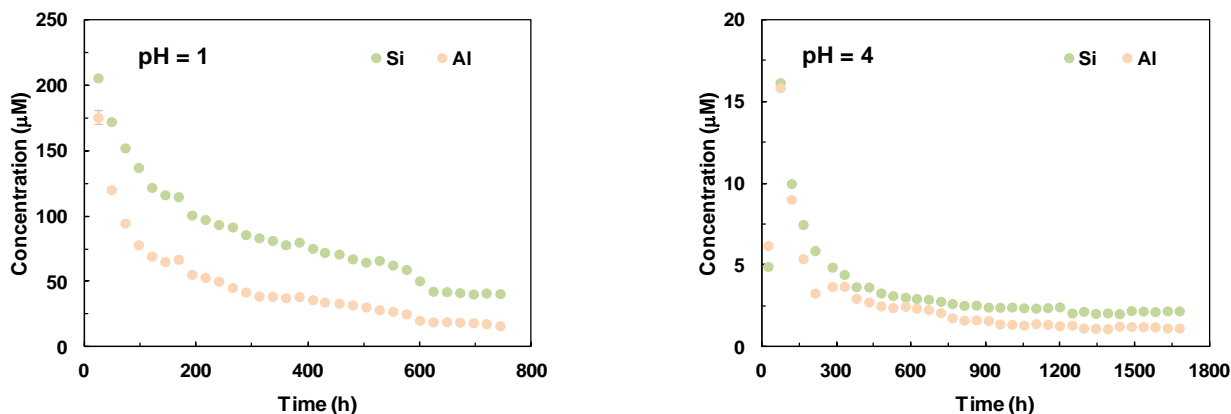


Fig. 1. Variation in Si and Al concentrations of the output solutions in experiments conducted at pH 1 and 4 and at 0.25 (M) ionic strength and 25°C.

A stoichiometric release of Al and Si has been reported for the dissolution of pure phyllosilicates under extremely acidic conditions (i.e. pH ≤ 3) (Bibi et al., 2011b; Kohler et al., 2003; Rozalen et al., 2008).

Table 1. Log-normalised dissolution rates ($\text{mol m}^{-2} \text{s}^{-1}$) of Bottle Bend clay sample calculated from Si, Al and Fe release at the steady state in the higher (0.25 M) and lower (0.01 M) ionic strength (*I*) solutions at pH 1–4 and 25°C.

Solution pH	<i>I</i> = 0.25 M			<i>I</i> = 0.01 M		
	R_{Si}	R_{Al}	R_{Fe}	R_{Si}	R_{Al}	R_{Fe}
1	-11.94	-12.29	-12.60	-11.91	-12.24	-12.46
2	-12.28	-12.55	-12.94	-12.11	-12.42	-12.58
3	-12.89	-13.18	-13.49	-12.77	-13.06	-13.38
4	-13.22	-13.48	-13.95	-13.18	-14.18	-14.21

The dissolution rates of clay (R_{Si} , R_{Al} and R_{Fe}) derived from the steady state release of Si, Al and Fe at pH range of 1 to 4 and at 25°C temperature for the ionic strength solutions are presented in Table 1. Clay dissolution rates decreased with an increase in the solution pH, a trend typically observed for clay dissolution in acidic solutions (Amram and Ganor, 2005; Bibi et al., 2011b). The dissolution rates of clay followed the order $R_{Si} > R_{Al} > R_{Fe}$. Similar R_{Si} values were obtained at the higher and lower ionic strength at corresponding pH values.

The R_{Al} value obtained at the higher ionic strength at pH 4 was significantly smaller than the R_{Al} value obtained at the lower ionic strength resulting from adsorption of dissolved Al on the mineral surfaces at the lower ionic strength. A similar effect of the ionic strength was reported for pure phase phyllosilicate dissolution in our earlier experiments (Amram and Ganor, 2005; Bibi et al., 2011a; Bibi et al., 2011b). The clay dissolution rates (R_{Si}) showed an increasing trend with an increase in the solution temperature from 25 to 45°C. By plotting log dissolution rates (R_{Si}) against $1/T$, E_{app} values at pH 1 and 4 were calculated using the Arrhenius equation (Fig. 2). The apparent activation energy values of 18.3 and 9.0 kcal mol⁻¹ were obtained at pH 1 and 4, respectively.

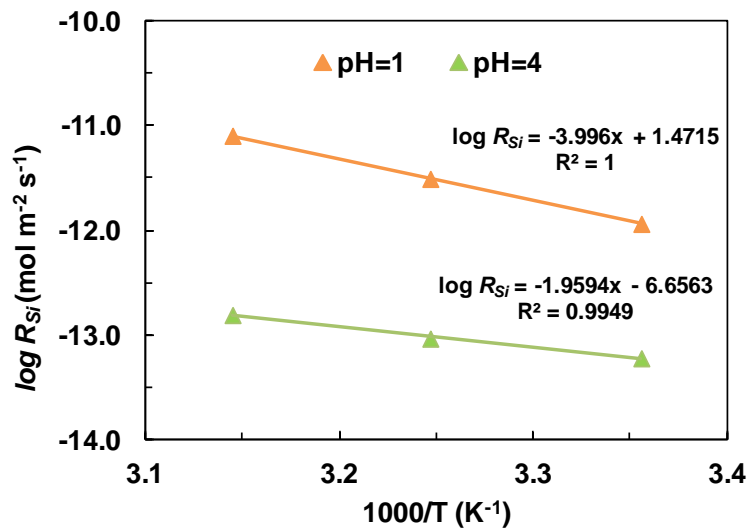


Fig. 2. Arrhenius plot illustrating the variation in steady state clay dissolution rate, $\log R_{Si}$ (mol m⁻²s⁻¹) against 1000 times reciprocal temperature, T (K⁻¹) for the experiments performed at pH 1 and 4.

The activation energies calculated in the present study showed similar pH dependence as those reported in previous studies on phyllosilicate dissolution (Carroll and Walther, 1990; Rozalen et al., 2009).

Conclusions

The clay dissolution rates derived from Si, Al and Fe release have shown a strong dependence on pH and temperature and in the case of Al also on the ionic strength. The R_{Al} values obtained at the higher ionic strength at pH 4 at all temperatures were significantly greater than R_{Al} values at the lower ionic strength at the corresponding pH due to the adsorption of dissolved Al on the mineral surface at the lower ionic strength. These findings suggest that the phyllosilicate dissolution under highly saline-acidic conditions ($I = 0.25$ M) particularly at pH = 4 results in enhanced dissolved concentrations of Al compared to low ($I = 0.01$ M) or non-saline acidic solutions; this may have an adverse effect on the associated systems in the form of Al³⁺ toxicity to plants or other adverse effects linked to the increased

availability of Al in the soil solution. The results from this study provide an insight into the dissolution behaviour of clay subject to saline-acid sulfate solutions in ASS and are useful to model geochemistry of these soils as a function of solution and environmental conditions.

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Notes