



## Kinetics of montmorillonite dissolution An experimental study of the effect of oxalate

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### ABSTRACT

Low molecular weight organic acids, ubiquitous in soils and sediments, play an important role in the alteration and weathering reactions as they enhance mineral dissolution rates. The dissolution rate of montmorillonite was measured in buffered oxalate solutions over a pH range from 3 to 8 and total oxalate concentrations of 0.1, 0.3 and 1.0 mmol L<sup>-1</sup> at 25 °C in a stirred flow-through reactor. Dissolution rates were obtained based on the release of Si at a steady state under far from equilibrium conditions. From pH 4 to 8, the addition of oxalate enhances the montmorillonite dissolution rate up to a maximum of 0.5 logarithmic units at pH 7 compared to the experiments in oxalate-free solutions. In order to understand the dissolution mechanism, oxalate adsorption was measured in batch experiments at pH 2–11 and Al speciation was modeled with EQ3NR. Oxalate adsorbs onto montmorillonite at pH < 8 up to 18 μmol g<sup>-1</sup> at the highest concentration studied. In addition, DR-FTIR spectroscopy was used to study the interaction of oxalate with montmorillonite. Two mechanisms were consistent with the experimental data: the formation of surface complexes between oxalate and aluminum sites on the surface of the montmorillonite edges, and the decrease of the activity of Al<sup>3+</sup> by formation of aqueous Al-oxalate complexes.

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### 1. Introduction

Low molecular weight organic acids are ubiquitous in soils and sediments, where vegetation and microbes introduce them. They can react with minerals in the Earth's crust and are known to play an important role in the alteration and weathering reactions at the mineral–water interface. In particular, they are implicated in the enhancement of clay mineral dissolution because of their ability to form metal–ligand complexes enhanced by the high surface area of clay minerals, and to increase the acidity of soils (e.g., Zitic and Stumm, 1984; Furrer and Stumm, 1986).

Recent evidence indicates that the dissolution reactions of phyllosilicates occur mainly on broken edge sites and are controlled by several factors including temperature, pH and the presence of organic ligands and inhibitors. Most studies agree that under the same pH conditions the dissolution rate is faster in the presence of organic ligands than that without (e.g., Zitic and Stumm, 1984; Furrer and Stumm, 1986; Carroll-Webb and Walther, 1988; Chin and Mills, 1991; Wieland and Stumm, 1992; Ganor and Lasaga, 1994; Oelkers and Schott, 1998; Stillings et al., 1998; Wang et al., 2005; Cama and Ganor, 2006; Golubev et al., 2006; Ramos et al., 2011). There is general agreement that the overall dissolution process is the result of several mechanisms that act simultaneously: proton-promoted (pH effect) and ligand-promoted dissolution. The ligand-promoted dissolution is affected

by i) the formation of surface Al–oxalate complexes that polarize and weaken the Al–O bonds and ii) the formation of Al–oxalate aqueous complexes that reduces the concentration of free Al<sup>3+</sup>. Depending on the concentration of Al in the solution, three situations can occur: 1) the formation, under far from equilibrium conditions, of aqueous Al–oxalate complexes that reduce the aqueous concentration of free Al<sup>3+</sup> and thus decrease Al inhibiting effect (Oelkers et al., 1994; Devidal et al., 1997; Oelkers and Schott, 1998); 2) the formation of aqueous Al-complexes near equilibrium that decrease the solution saturation state with respect to montmorillonite and subsequently the impact of the reaction chemical affinity on dissolution rate; and 3) inhibition of gibbsite precipitation that could reduce the montmorillonite reactive surface area via the decrease of free Al<sup>3+</sup> due to the formation of aqueous Al–oxalate complexes. Which mechanism prevails in the presence of organic ligands is still under debate.

Montmorillonite was chosen in this study because it is a ubiquitous mineral in soil and its dissolution mechanism and reactivity have been widely investigated in previous work (Furrer et al., 1993; Zysset and Schindler, 1996; Bauer and Berger, 1998; Cama et al., 2000; Huertas et al., 2001; Amram and Ganor, 2005; Metz et al., 2005a,b; Rozalén et al., 2008, 2009a,b; Ramos et al., 2011). Furthermore oxalate, the organic ligand of interest in this study, is an abundant low molecular weight organic acid in surface environments, as a result of its exudation by plant roots and fungi (Gadd, 1999; Ryan et al., 2001). For example, in forest soils oxalate concentration in the soil solutions can range from 25 to 1000 μM (Gadd, 1999). Oxalate exhibits a strong capacity to enhance significantly the dissolution rate of aluminosilicates and aluminum

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oxides (Zutic and Stumm, 1984; Furrer and Stumm, 1986; Chin and Mills, 1991; Wieland and Stumm, 1992; Welch and Ullman, 1993; Pokrovsky et al., 2005; Wang et al., 2005; Cama and Ganor, 2006; Golubev and Pokrovsky, 2006; Golubev et al., 2006; Olsen and Rimstidt, 2008).

The adsorption and organic acid-induced dissolution in phyllosilicates has been investigated by batch adsorption experiments (Ward and Brady, 1998; Lackovic et al., 2003; Kang and Xing, 2007; Kitadai et al., 2009b). Batch equilibrium and adsorption edge studies provide useful information about the role of organic ligands in clay dissolution studies. These macroscopic methods are incapable, however, of providing mechanistic insight of the organic ligand–clay interactions (Johnston and Sposito, 1987). In the study of organic ligands and their interaction with clay minerals, vibrational spectroscopy has been applied successfully. Attenuated total reflectance (ATR) and diffuse reflectance (DR) FTIR methods, in particular, have been extensively used to investigate the bonding mechanism of organic ligands to clays as well as to oxides to examine surface complexation (inner-sphere or outer-sphere complexation), and the stoichiometry of the surface interaction (monodentate or polydentate, mononuclear or polynuclear) (Biber and Stumm, 1994; Kubicki et al., 1997; Nordin et al., 1997; Nordin et al., 1998; Kubicki et al., 1999; Specht and Frimmel, 2001; Lackovic et al., 2003; Johnson et al., 2004; Yoon et al., 2004; Kang and Xing, 2007; Noren and Persson, 2007; Ha et al., 2008; Noren et al., 2008; Kitadai et al., 2009a,b; Jonsson et al., 2010).

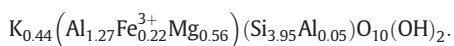
The objective of this study is to investigate the role of oxalate on the montmorillonite dissolution reaction. Dissolution rates are derived from flow-through dissolution experiments in buffered oxalate solutions. Moreover, the adsorption of the oxalate on montmorillonite was approached by batch adsorption experiments and through DR-FTIR spectroscopy.

## 2. Materials and methods

### 2.1. Materials

The clay material used in this study was a bentonite from the La Serrata–Cortijo de Archidona deposit located at Cabo de Gata (Almería, SE Spain). This bentonite is approximately 92% montmorillonite; the rest consists of accessory/companying minerals (quartz, feldspars, micas, calcite, amphibole) and volcanic glass (for a detailed characterization of the sample and methods see Rozalén et al., 2008). The experiments were performed on the <4 μm fraction, collected by repeated sedimentation–suspension cycles in deionized water, and then exchanged with K<sup>+</sup> ions.

The calculated structural formula of the K-smectite (based on half unit cell) corresponds to a montmorillonite:



Only 0.38 K<sup>+</sup> ions per half formula unit are exchangeable which indicates the presence of a small proportion of non-swelling layers. X-ray diffraction (XRD) patterns recorded on powder specimens and on oriented and glycolated mounts indicate that the sample is composed of a dioctahedral smectite with approximately 10–15% non-swelling layers. No accessory phases were detected. The specific surface area was measured by BET (Brunauer et al., 1938), using 5-point N<sub>2</sub> adsorption isotherms, after degassing the sample for two days at 110 °C under vacuum. The specific surface area was 111 m<sup>2</sup> g<sup>-1</sup>, with an associated uncertainty of 10%.

### 2.2. Flow through dissolution experiments

Dissolution experiments were performed in single-pass, stirred, flow-through cells which facilitated the measurement of the dissolution

rate under fixed saturation state conditions by modifying flow rate, initial sample mass and input solution concentrations. The reactors were fully immersed in a thermostatic water-bath held at a constant temperature of 25 ± 1 °C. The flow rate was controlled with a peristaltic pump that injects the input solution into the bottom chamber of the cell (0.02 mL min<sup>-1</sup>) where the solution is homogenized with a magnetic stirrer before reaching the upper chamber. The solid sample is confined within the upper chamber (reaction zone) by using two membrane filters: a 5 μm nylon mesh plus a 1.2 μm Durapore membrane at the bottom and a 0.45 μm Durapore membrane at the top. The total volume of the cell was 46 mL and the solid mass added to each cell was approximately 0.1 g, to yield a solid solution ratio of approximately 2 g L<sup>-1</sup>.

Buffer solutions were prepared using sodium oxalate in concentrations of 0.03, 0.1 and 1.0 mmol L<sup>-1</sup>. In the experiments, 10 mmol L<sup>-1</sup> KNO<sub>3</sub> was used as background electrolyte concentration. The pH was adjusted from 3 to 8 by adding HNO<sub>3</sub> or KOH solutions. Sodium azide (NaN<sub>3</sub>, 2 ppm) was added as bactericide. No smectite structural cations (Si, Al, Mg, Fe) were added to the input solutions.

In each run, the flow rate and the input pH were held constant until steady-state conditions were achieved. The steady state was assumed to prevail when the Si output concentration remained fairly constant, differing by less than 6% between consecutive samples (Rozalén et al., 2008). Reaction times were from 800 to 1200 h depending on the pH and oxalate concentration. At steady state, dissolution is expected to proceed under far-from-equilibrium conditions. All the experiments consisted of a single stage; the cell was dismantled after the steady state was achieved.

After sampling every 24 h, the pH of the output solutions were immediately measured at room temperature by using a Crison combination electrode standardized with pH 4.01 and 7.00 buffer solutions. The reported accuracy was 0.02 pH units. An aliquot was separated for oxalate analysis. Then the output solutions were acidified to pH 3 with HNO<sub>3</sub> to prevent the precipitation of Al- or Fe-bearing phases during storage for further analyses.

The Si concentration in the samples was determined by colorimetry by using the molybdate blue method (Grasshoff et al., 1983). Total Al, Fe and Mg concentration in the solutions at steady-state conditions was determined by inductively coupled plasma mass spectrometry (ICP-MS) in a Hewlett Packard 4500 series spectrometer. The concentration of oxalate was measured by ion chromatography (IC) using a Metrohm 761 Compact Ion Chromatograph with a Metrosep A Supp 4-250 column with chemical suppression. The eluent was prepared with 1.7 mmol L<sup>-1</sup> NaHCO<sub>3</sub> and 1.8 mmol L<sup>-1</sup> NaCO<sub>3</sub>. The detection limits are 5 ppb for Si, 0.3 ppb for Al, 0.3 ppb for Mg, 3 ppb for Fe and 0.9 ppm for oxalate. The associated errors were 5% for Si and Al, 3% for Mg and Fe, and 5% for oxalate.

In a well-mixed, flow-through reactor the dissolution rate, *Rate* (mol g<sup>-1</sup> s<sup>-1</sup>), can be calculated based on the mass balance of a given mineral component *j*. Under steady-state conditions this is given by the following equation (e.g., Rozalén et al., 2008):

$$Rate(mol\ g^{-1}\ s^{-1}) = -\frac{1}{\nu_j} \frac{q}{M} (C_{j,out} - C_{j,in}), \quad (1)$$

where  $\nu_j$  is the stoichiometric coefficient of component *j* in the dissolving mineral, *q* stands for the volumetric fluid flow through the system, *M* is the mass of smectite and  $C_{j,out}$  and  $C_{j,in}$  correspond to the concentrations of component *j* in the output and input solutions, respectively. The rate is defined as negative for dissolution and positive for precipitation. In this study the dissolution rate is calculated from the Si and Al concentrations ( $R_{Si}$  and  $R_{Al}$ ) in the output solutions. All dissolution rates were normalized to the initial mass of smectite. The error in the calculated rate is estimated by using the Gaussian error propagation method and is less than 6% in all cases, which corresponds to approximately 0.1 logarithmic units.

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