Dissolution of beidellite in acidic solutions: Ion exchange reactions and effect of crystal chemistry on smectite reactivity

Valentin Robin [a,b,*], Emmanuel Tertre [a], Olivier Regnault [b], Michael Descostes [b]

[a] *Université de Poitiers/CNRS, UMR 7285 IC2MP, équipe HydrASA, Bat. B8 rue Albert TURPAIN, TSA 51106 – 86073 Poitiers CEDEX 9, France*
[b] *AREVA Mines, Research and Development Department, Tour AREVA, 1, place Jean Millier, 92084 Paris La Défense Cedex, France*

Abstract

The dissolution rate of beidellite, a dioctahedral smectite with tetrahedral charge that is a common swelling clay mineral in surface and subsurface natural environments, was studied in acidic solutions at 25 °C under far from equilibrium conditions. A <0.3 μm size fraction of SBId1 beidellite ($(Si_{7.148}Al_{0.852})(Al_{3.624}Mg_{0.18}Fe(III)_{0.224})O_{20}(OH)_4M^+_{0.948}$) purchased from the Clay Mineral Society was used as the starting material, and experiments were performed in stirred flow-through reactors using HCl solutions with pH values ranging from 1 to 3. Several hydrodynamic conditions were tested using different flow rates with stirred and non-stirred particles. The aqueous Al/Si ratio measured at the outlet of the reactor was followed as a function of time and compared to solid stoichiometry values to assess the mechanisms occurring at the solid/solution interface. The reversible adsorption of Al^{3+} in the smectite interlayer space was evidenced for pH > 1.1, and the presence of an amorphous Si-enriched layer can be reasonably assumed in some cases from the interpretation of the aqueous concentrations and the characterization of the solid phase (X-ray diffraction and FTIR spectroscopy). Beidellite dissolution rates normalized to the sample mass ($mol\ g^{-1}\ s^{-1}$) were obtained from Si and Al concentrations under steady state dissolution conditions. Calculated rates were compared with those previously reported for montmorillonite in several publications. The beidellite dissolution rates are, on average, ten times lower than those of montmorillonite. This implies that the smectite crystal chemistry (i.e., amount of Al^{3+} versus Mg^{2+} or Fe^{3+} substitution in the structure) has a strong effect on its stability and should be considered in reactive transport models in which the dissolution properties of smectites are taken into account.

1. INTRODUCTION

Swelling clay minerals such as smectites are present in a wide range of different natural environments, from soils to sediments and rocks (Meunier, 2005). Due to their intrinsic properties such as their high cation exchange capacity (CEC) and low permeability, smectite reactivity has been widely studied in many contexts related to the mobility of contaminants in soils and sediments (Pabalan and Turner, 1997; Lu et al., 2014), waste disposal (Tertre et al., 2005) and mining and industrial sites (Robin et al., 2015a). However, the durability of smectites and the preservation of their intrinsic properties during changes in physico-chemical conditions (pH, temperature or salinity variations) should be considered. Dissolution rates of smectites have therefore been studied using different experimental designs, such as batch (Zysset and Schindler, 1996; Bauer and Berger, 1998; Huertas et al., 2001; Rozalén et al., 2008), column (Gainey et al., 2014) and stirred flow-through reactors (Amram and Ganor, 2005; Yokoyama et al., 2005; Metz

* Corresponding author at: Université de Poitiers/CNRS, UMR 7285 IC2MP, équipe HydrASA, Bat. B8 rue Albert TURPAIN, TSA 51106 – 86073 Poitiers CEDEX 9, France. Tel.: +33 (0)5 49 45 42 86.
E-mail address: valentin.robin@univ-poitiers.fr (V. Robin).

et al., 2005a; Rozalén et al., 2008; Marty et al., 2011). Using this last design, smectite dissolution rates were investigated as a function of pH, temperature and ionic strength. Smectite dissolution rates decrease with increasing pH from 1 to 5 (Marty et al., 2014 and references therein). In most studies, the smectite used as starting material belongs to the montmorillonite group. According to the AIPEA nomenclature committee, the montmorillonite group is defined as natural lamellar silicates that are composed of two tetrahedral sheets (silica) sandwiching an octahedral sheet (dioctahedral aluminum hydroxide) constituting the so-called TOT layer. The structural charge of these minerals ranges from 0.4 to 1.2 per unit cell ($/O_{20}(OH)_4$) and is mainly due to isomorphic substitutions of aluminum by magnesium in the octahedral sheets (Guggenheim et al., 2006). Aluminum substitutions by ferric iron in the octahedral sheets are also common in these swelling clay minerals, but do not imply any change in the structural charge. However, minerals belonging to the montmorillonite group are only a subfraction of the smectitic minerals. Indeed, the smectite family is composed of several minerals differing in their octahedral sheet occupancy (di or trioctahedral minerals), charge location (tetrahedral or octahedral charge) and the nature of the isomorphic substitutions occurring in their crystal structure. To our knowledge, the effect of smectite crystal chemistry on their dissolution properties in acidic conditions has been poorly studied (Breen et al., 1995; Gainey et al., 2014). The results reported by Breen et al. (1995) demonstrate that the reactivity of the octahedral sheet of montmorillonite under highly acidic conditions (1 mol L^{-1} H$_2$SO$_4$ – 95 °C) is significantly dependent on the layer charge. With respect to other minerals of the dioctahedral smectite group, the dissolution rates of nontronite (Fe^{3+}-rich smectite with the main charge located in the tetrahedral sheets) and montmorillonite were recently compared (Gainey et al., 2014). The authors present dissolution rates of nontronite that are higher than those of montmorillonite (by 2–30 times) and explained their variation by the higher stability of montmorillonite characterized by a high amount of Al^{3+} relative to Fe^{3+}. However, the solid/solution ratios, residence times and experimental designs (column versus stirred flow-through reactors) used to obtain these data with these two materials differed. Therefore, the order of magnitude reported by the authors of the crystal chemistry effect on the dissolution rate of smectite remains to be confirmed. For other types of dioctahedral smectites, such as beidellite (Al-rich smectite with tetrahedral charge and low Fe and Mg contents), no data have been reported concerning their dissolution far from equilibrium conditions to our knowledge. The investigation of the dissolution rate of this Al-rich pole could be particularly relevant to probing the effect of the crystal chemistry on the dissolution rates of smectites.

This paper reports for the first time dissolution rates of beidellite in acidic conditions in stirred flow-through reactors. Comparing the data obtained in this study for beidellite with data available in the literature for montmorillonites affords discussion of the effect of smectite crystal chemistry on its stability under acidic conditions. A specific experiment was performed with a montmorillonite that had been previously studied in the literature to validate our experimental design. Experiments with beidellite were then performed with the SBId1 reference beidellite from the clay source repository of the Clay Mineral Society. Dissolution rates of <0.3 μm-Na$^+$ saturated particles were obtained at 25 °C and pH 1–3 using hydrochloric acid. Particular attention was paid to the characterization of the solid isolated from the experiments using XRD and FTIR spectroscopy. Such measurements allow the interpretation of the aqueous data and the probing of the mechanisms associated with dissolution, such as cation exchange and neoformation.

2. MATERIALS AND METHODS

2.1. Characterization of the solid

The smectites used in this study were reference beidellite (SBId-1) and montmorillonite (SAz-1) obtained from the Clay Minerals Society, Source Clay Repository (Department of Agronomy, Purdue University, West Lafayette, IN, USA). More information on the geological origin of these two clay minerals can be found in Moll (2001) and Post et al. (1997). The structural formula (Si$_{7.148}$Al$_{0.852}$)(Al$_{3.624}$Mg$_{0.18}$Fe(III)$_{0.224}$)O$_{20}$(OH)$_4$M$^+_{0.948}$ of the SBId-1 beidellite reported by Gailhanou et al. (2012) shows that the main isomorphic substitutions are located in the tetrahedral sheet (more than 80%). A size fraction of less than 0.3 μm (i.e., equivalent diameter) was collected using the method described in Robin et al. (2015a). Impurities are present at a maximum proportion of 5 wt% for both kaolinite and illite/smectite (I–S) interstratified minerals. The BET specific surface area of the <0.3 μm fraction obtained is equal to 70 ± 5 m^2 g^{-1} (Robin et al., 2015a). To validate our interpretations of the crystal chemistry effects on dissolution rates, we verified that the data obtained for a montmorillonite with our experimental design are similar to those previously published (Amram and Ganor, 2005). The structural formula of SAz-1 montmorillonite obtained from the analysis reported by Metz et al. (2005a) on the same purified material that that used in this present study is (Si$_{7.87}$Al$_{0.13}$)(Al$_{2.75}$Fe(III)$_{0.15}$Mg$_{1.10}$)O$_{20}$(OH)$_4$M$^+_{1.23}$. This montmorillonite displays a structural charge close to that of SBId1 beidellite (1.23 against 1.03 per unit cell), but with substitutions mainly in the octahedral sheet. Size fractionation was performed according to the protocol proposed by Metz et al. (2005b) to obtain an average equivalent diameter close to 0.7 μm. The specific surface area of the SAz-1 sample was measured using the BET-N$_2$ method (Brunauer et al., 1938), as for the beidellite sample, and was found to be 90 ± 5 m^2 g^{-1}, which is within the range of 34 to 97 m^2 g^{-1} reported in the literature for SAz1 samples (Pabalan and Turner, 1997; Metz et al., 2005b and references therein).

2.2. Flow-through experiments

Dissolution experiments were carried out in stirred flow-through reactors (35 mL in volume) similar to those used in previous smectite dissolution experiments (Cama et al., 2000; Amram and Ganor, 2005; Metz et al., 2005a; Rozalén et al., 2008; Marty et al., 2011). The reactor was