

# The kinetics of smectite dissolution

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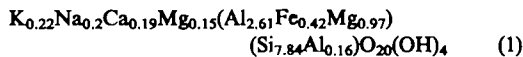
A.C. Lasaga

## Introduction

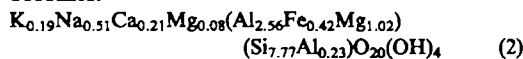
Little is known about the dissolution rate of smectite in general, and its dependence on the degree of saturation. Furrer *et al.* (1993) measured the dissolution rate of montmorillonite as a function of pH under acidic conditions. However, their Al and Si results were not stoichiometric. The main goal of the present study is to measure the stoichiometric dissolution rate of a smectite under alkaline conditions (pH = 8.8) and various degrees of saturation state at 80°C.

## Materials and methods

The smectite used in this study is a bentonitic smectite from the Neogene Cabo de Gata volcanic deposit, Spain, furnished by J. Cuadros and J. Linares (CSIC). Based on the whole rock composition of the sample, and assuming that only smectite is present in the rock, the structural formula is:



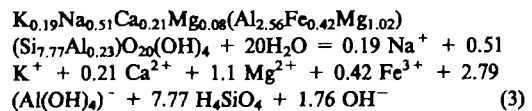
In order to achieve stoichiometric dissolution, the smectite was equilibrated for about 2 months in a 0.01 M Borax ( $\text{Na}_2\text{B}_4\text{O}_7$ ) solution. As a result of this pretreatment the interlayered concentration of Na was doubled and the structural formula becomes:



Two types of experiments were carried out: Flow-through experiments to measure the dissolution rate and batch experiments to evaluate the equilibrium constant. Flow-through experiments were carried out using a stirred-flow reactor that was fully immersed in a water bath held at  $80 \pm 0.02^\circ\text{C}$  (Nagy *et al.*, 1991; Ganor *et al.*, 1994). The batch experiments were carried out in Teflon bottles in the same water bath. The degree of saturation of each experiment was varied by adding various amounts of Si to a 0.01 M borax input solution and by varying the initial mass of smectite and the flow rate.

## Calculations

The overall dissolution reaction of smectite under alkaline pH conditions is:



At steady state, the dissolution rate,  $R$ , ( $\text{mole m}^{-2} \text{sec}^{-1}$ ) in a well-mixed flow-through experiment is obtained from the expression:

$$R = -q(C_{\text{out}} - C_{\text{inp}})/(v_j A) \quad (4)$$

where  $C_{\text{inp}}$  and  $C_{\text{out}}$  are the concentrations of component  $j$  in the input and the output,  $v_j$  is the stoichiometric coefficient of  $j$  in the dissolution reaction,  $A$  is surface area and  $q$  is the fluid volume flux through the system. The analytical error in the rate calculated from this equation is  $\pm 15\%$  and is dominated by the uncertainty of the BET surface area measurement ( $\pm 10\%$ ). The degree of saturation of the solution with respect to smectite (equation (2)) is calculated in terms of the Gibbs free energy of reaction ( $\Delta G$ ),

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

where  $R$  is the gas constant,  $T$  is the absolute temperature and  $IAP$  and  $K_{eq}$  are actual and equilibrium ion activity products of the solution, respectively.

## Results and discussion

**Equilibrium Constant of Smectite Dissolution Reaction:** The batch experiments are used to determine the equilibrium constant of the smectite dissolution reaction. The thermodynamic treatment of the batch experiments is applicable once a solution composition has been established to be in 'equilibrium' with smectite. Future experiments (both flow-through and batch) should establish the validity of this equilibrium assumption in a more cogent fashion by varying the initial conditions (supersaturated as well as

undersaturated) of the solutions. From the final solution composition, the calculated equilibrium constant for the smectite composition given in equation (2) at 80°C is  $K_{sp} = 1.2 \pm 0.8 \times 10^{-63}$ .

**Smectite Dissolution Rate:** Al, Si and Mg analyses of the output solutions at steady state show congruent smectite dissolution in most of the experiments in which Si input concentration is less than 100  $\mu\text{M}$ . Here we will discuss only these congruent results. The average molar ratios, Al/Si, Mg/Al and Mg/Si from the dissolution are  $0.35 \pm 0.04$ ,  $0.41 \pm 0.02$  and  $0.140 \pm 0.006$ , respectively, which are in agreement with the stoichiometric molar ratios of 0.36, 0.39 and 0.141 for the smectite composition in equation (2). On the other hand, Fe, Ca and K demonstrate non-stoichiometric dissolution. In other words, all cations belonging to the octahedral and tetrahedral layers of the smectite, except Fe, display stoichiometric dissolution. Since we see a stoichiometric release of octahedral Mg and Al, it is safe to assume that there is a stoichiometric release of  $\text{Fe}^{3+}$ , the other octahedral ion, as well. However, we can not determine the  $\text{Fe}^{3+}$  because it is probably instantaneously removed from solution by precipitation of another solid such as  $\text{Fe}(\text{OH})_3$ . The stoichiometric dissolution of the octahedral and tetrahedral layers implies that those interlayer cations should also be released to the solution. The non-stoichiometric behavior of the Ca and K probably indicates that, in addition to the release of the interlayer cations to the solution there is rapid exchange of Ca and K with the exchangeable cations in smectite. An alternative explanation for the non-stoichiometric release of the Ca may be that the Ca concentration is buffered by the carbonate system. Further more, some of the K may be contained in illite that is present in the sample in very small amount, and which is assumed to dissolve more slowly than the smectite. The stoichiometric release of structural smectite ions rules out significant smectite to illite transformation during the experiments. Production of illitic layers would involve a change in the composition of the bulk solid and subordinate non-stoichiometric ion release. We relate the achievement of stoichiometric dissolution in this study to the two months of pretreatment of the smectite before the experiment. We suggest that incongruent smectite dissolution may be an artifact of inadequate surface preparation, as was suggested for kaolinite by Nagy *et al.* (1991).

Fig. 1 plots the dissolution rate versus the degree of saturation calculated in terms of the Gibbs free energy of reaction  $\Delta G$ . The dissolution rate is slower as the solution composition

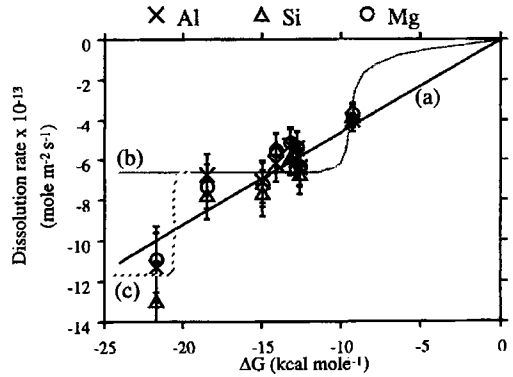


FIG. 1.

approaches equilibrium. In the  $\Delta G$  range of  $-15$  to  $-18$  kcal/mole the dissolution rate is constant. However, the most undersaturated experiment shows a much faster dissolution rate, which may indicate that the experiments did not approach the dissolution plateau (Lasaga *et al.*, 1994). The flow rate in this experiment is twice the flow rate of the other experiments. An alternative explanation may be that we approach the dissolution plateau, but the rate is faster as a result of an effect of the flow rate on the dissolution rate. While the data in figure 1 certainly show a significant dependence on  $\Delta G$ , the exact functional dependence is not clear yet because of lack of more data nearer equilibrium. Interestingly, the data in figure 1 can all be fitted to a straight line going through 0 at equilibrium (line (a)). However, based on all our earlier work, we suspect that the rise from the dissolution plateau will be more non-linear as in curve (b). An unusual third possibility is that there are two plateaus as in curve (c). Possible interpretations will be discussed at the meeting.

## References

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