The effects of oxalic acid on kaolinite dissolution rate

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Introduction

The role that dissolved organic acids in groundwaters and soils play in geochemical processes has attracted considerable attention in the last decade. Organic chelation of dissolved metals enhance the solubility of various minerals. Adsorption of organic anions on mineral surfaces catalyzes the dissolution and precipitation of minerals. The goals of the present study are to determine the reaction mechanism and the degree of enhancement of kaolinite dissolution rate in the presence of oxalic acid.

Materials and methods

The kaolinite used in this study is from Dry Branch, Georgia. We have found that pretreatment of mineral surfaces is necessary to obtain reliable and stoichiometric kinetic results (e.g., Nagy et al., 1991; Ganor et al., 1994).

Experiments were carried out using a stirred-flow reactor that was fully immersed in a water bath held at a constant temperature of 80°C (Nagy et al., 1991; Ganor et al., 1994). Input solutions were prepared with a specific oxalic acid concentration by diluting concentrated oxalic acid with distilled, deionized water. Variable amounts of $HClO_4$ or NaOH were added to the solution in order to set the input pH to values around 3.

Results and discussion

Dissolution rates at steady state and the Gibbs free energy of reaction (ΔG) were calculated as described by Ganor et al. (1994).

To understand the mechanism by which the oxalate concentration influences the rate, one should separate this effect from effects of other parameters such as output pH, and Si and Al concentration. A general rate law for a single mechanism of heterogeneous mineral surface reactions can be written as (Lasaga et al., 1994):

$$\text{Rate} = K_0 \cdot A_{\min} \cdot e^{-Ea/RT} \cdot a_{H^+}^{n_{H^+}} \cdot \prod_i a_i^{n_i} \cdot f(\Delta G) \quad (1)$$

where k_0 is the rate constant, $A_{\min}$ is the reactive surface area of the mineral, E_a is the activation energy of the overall reaction, a_j is the activity of species j in the solution and $f(\Delta G)$ is a function of the Gibbs free energy. Terms involving activities of species in solution (such as oxalate species), a_i, incorporate possible catalytic or inhibitory effects on the overall rate. Such catalysis or inhibition is kinetically quite distinct from the final term, $f(\Delta G)$, which accounts for the important variation of the rate with deviation from equilibrium.

Equation (1) describes a general rate law if *one mechanism* is dominant throughout all experiments. However, at least two mechanisms must be considered when discussing the kaolinite dissolution in the presence of oxalic acid. The first is the oxalate-promoted (*oxp*) dissolution mechanism and the second is the proton-promoted (*pp*) dissolution mechanism (Ganor et al., 1994). The average dissolution rate in the absence of oxalate is $2.6 \pm 1.3 \times 10^{-12}$ mole m^{-2} sec^{-1}. In comparison, when the oxalate concentration is 117μM, the dissolution rate is $7.8 \pm 0.6 \times 10^{-12}$. Under these conditions, the contribution of the proton-promoted mechanism to the overall dissolution rate should not be ignored. Therefore, the dissolution rate is the sum of two terms:

$$\text{Rate} = \text{Rate}_{pp} + \text{Rate}_{oxp} \quad (2)$$

Each of these terms has a similar form to the one in equation (1).

Based on equation (1), two explanations may be suggested for the increase in dissolution rate as a function of oxalate concentration. The first explanation is that one (or more) of the oxalate species is adsorbed on the kaolinite surface and permits the system to follow a faster parallel reaction path. We refer to this as the oxalate-promoted dissolution mechanism. The second explanation is that the oxalate decreases the degree of saturation with respect to kaolinite dissolution (ΔG) and as a result the dissolution rate increases. Enhancement of the dissolution rate as a result of changes in the degree of saturation may influence *both* the *oxp* and the *pp* mechanisms.

Enhancing dissolution rate by oxalate as a result of its effect on Al speciation and on ΔG. The rate
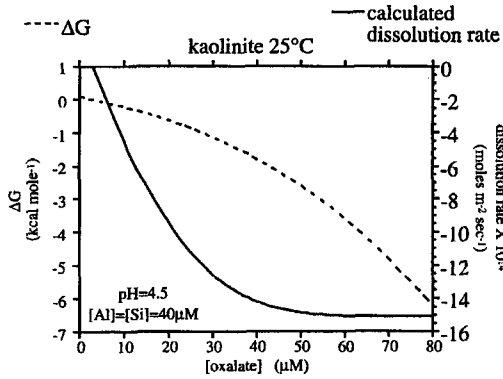
FIG. 1.

FIG. 2.

law for the proton-promoted dissolution mechanism ($Rate_{pp}$) of kaolinite in the pH range of 3−4 and 25−80°C is given by (Ganor *et al.*, 1994):

$$Rate_{pp} = 10^{-5.7\pm0.7} \cdot e^{-3500\pm550/T} \cdot a_{H^+}^{0.40\pm0.14} \cdot [-(1 - e^{(\Delta G/RT)^{0.9\pm0.3}})]$$

(3)

where the last term (in square brackets) of equation (3) is the non-linear $f(\Delta G)$ function observed originally by Nagy *et al.*, (1991) for kaolinite at pH = 3 and 80°C.

The calculated ΔG for a typical solution composition as a function of the oxalate concentration is shown in Fig. 1. The ΔG value decreases as the oxalate concentration increases and the solution becomes more undersaturated. The ΔG values allow us to calculate the effect of oxalate on the proton-promoted kaolinite dissolution rate, i.e., a theoretical case in which the reaction is not directly catalyzed by any oxalate species, so that equation (3) can be used. Fig. 1 shows a sharp increase in the calculated proton-promoted dissolution rate when the oxalate concentration increases from 4−30μM. Further increase of oxalate concentration above 50μM will not influence the dissolution rate, because the solution is on the dissolution plateau ($\Delta G < -2.5$ kcal/mole) and the dissolution rate is ΔG-independent.

The oxalate-promoted dissolution mechanism. The oxalate-promoted dissolution rate (R_{oxp}) is determined from the difference between the measured rate and the calculated proton-promoted rate (see equation 2 and 4). For all experiments $\Delta G \ll -2.5$ kcal/mole. Assuming that $f(\Delta G)$ for the oxalate-promoted dissolution mechanism is similar to that of equation (3), all experiments were conducted on the dissolution
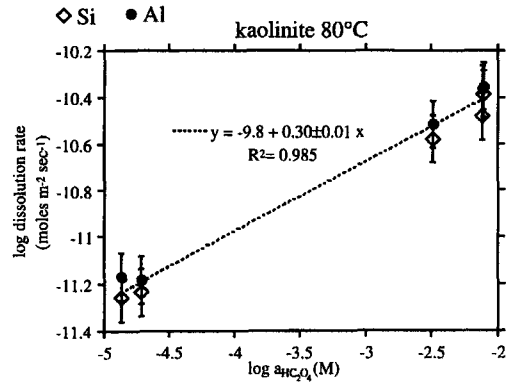
plateau and so, the dissolution rate is independent of ΔG. If we further assume that the oxalate-promoted mechanism is not influenced by changes in pH (i.e., $n_{H^+} = 0$), at constant temperature, equation (1) becomes

$$Rate_{oxp} = -k \cdot A_{min} \cdot a_{ox}^{n_{ox}}$$

(4)

where k is a new coefficient that includes the other constant terms. The dominant free oxalate species under the experimental conditions is $HC_2O_4^-$ (>85%). Fig. 2 plots the log of the oxalate-promoted dissolution rate as a function of log $a_{HC_2O_4^-}$. The reaction order with respect to $a_{HC_2O_4^-}$ is calculated from the slope of the linear trend in Fig. 2 to be $n_{HC_2O_4^-} = 0.30 \pm 0.01$.

Conclusions

Oxalate increases the kaolinite dissolution rate. This increase in rate is a result of *both* changing the degree of saturation and formation of complexes on the kaolinite surface. The enhancement of rate as a result of changing the degree of saturation is in effect only near equilibrium, and will affect both the proton-promoted and the oxalate-promoted dissolution mechanisms.

References

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