

Reactivity of Fe(II) in presence of calcite and Fe/CaCO₃ solid-solution

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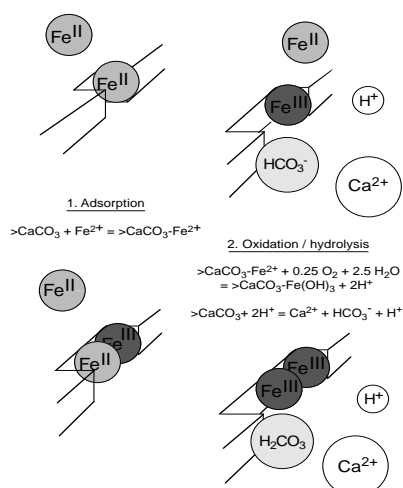
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Iron is a redox active element and it takes part in many processes like degradation and adsorption of inorganic and organic contaminants. Despite of its importance in aquatic systems its interactions with carbonaceous minerals (calcite) has hardly been studied.

The interaction of Fe(II) and calcite was investigated in absence and in presence of oxygen. *In absence of oxygen*, Fe(II) is efficiently sorbed by calcite. With ongoing equilibration of Fe(II) with calcite a mixed Fe/CaCO₃ phase is gradually formed, which contains 0.4% (mol/mol) Fe(II) under the applied experimental conditions (10 μM Fe(II), 1 g/L calcite, pH 7, saturated with regard to CaCO₃).

Oxygenation of Fe(II) is accelerated in the presence of calcite compared to the homogeneous reaction, if the metal ion is added directly to an aerated suspension (no equilibration). The same reactivity is observed throughout, even after the initially available reactive sites have been used up (the amount of reactive sites were determined from sorption experiment). We hypothesize a continuous reformation of reactive sites by dissolution of CaCO₃ in the vicinity of the formed Fe(III). The necessary acidity is produced by the hydrolysis of Fe(III) to Fe(OH)₃ (see Figure below).

If an equilibration of Fe(II) with calcite precedes the oxygen addition, no enhancement of the rate of oxidation by the surface is observed. In contrary, part of the Fe(II) incorporated as mixed Fe/CaCO₃ phase can not be oxidized by oxygen, even if exposed to it for several days.



Dependence of smectite dissolution rate on deviation from equilibrium

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The functional dependence of the dissolution / precipitation rate on the deviation from equilibrium expressed as Gibbs free energy of reaction, $f(\Delta G_r)$, is essential to any attempt to apply kinetic data to natural processes or to processes in nuclear waste repositories. An open question is whether the term $f(\Delta G_r)$ depends on environmental variables such as pH and temperature. To date, the $f(\Delta G_r)$ functionality has been experimentally tested at different conditions only for dissolution of gibbsite (Nagy and Lasaga, 1992; Mogollón et al., 1994). Here, we report on the extension of the ΔG_r effect on smectite dissolution rate at different pH and temperature. We carried out flow-through experiments with two montmorillonitic smectites, one at pH 3 and 50°C and the other at pH 8.8 and 80°C, to determine the ΔG_r effect on dissolution rate. At basic pH, ΔG_r varied between -3 and -31 kcal mol⁻¹, and at acid pH between -12 and -43 kcal mol⁻¹. At steady state, stoichiometric release was observed for the major tetrahedral and octahedral cations Si, Al and Mg. Following the reasoning of Nagy and Lasaga (1992), the dependency of rate on deviation from equilibrium is described by fitting the experimental data to a TST-type function. Fitting of the 80°C, pH 8.8 and the 50°C, pH 3 data results in Eqns. (1) and (2), respectively,

$$1. \quad \text{Rate} = -k \cdot \left(1 - \exp \left(-6 \cdot 10^{-10} \cdot \left(\frac{\Delta G_r}{R \cdot T} \right)^6 \right) \right)$$

$$(2) \quad \text{Rate} = -k \cdot \left(1 - \exp \left(-2 \cdot 10^{-8} \cdot \left(\frac{\Delta G_r}{R \cdot T} \right)^5 \right) \right)$$

where k (mol m⁻² s⁻¹) is a rate coefficient, R is the gas constant, T is temperature (K), and Rate is calculated in units of mol m⁻² s⁻¹. Several important implications can be drawn: far from equilibrium ($\Delta G_r < -30$ kcal mol⁻¹) rates are independent of deviation from equilibrium, as was assumed in Cama et al. (2000); near equilibrium the rate strongly depends on ΔG_r ; both equations (1) and (2) may be used to describe the two data sets, regardless of differences in pH, temperatures, and smectite samples.

References

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