Comparison between actual and theoretical dissolution rates in a granite–water interaction experiment at 180°C and 14 bar

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Introduction

The precise understanding of the processes controlling rate of mineral dissolution is crucial for modeling water–rock interaction in hydrothermal systems. Many theoretical approaches have been developed. The transition state theory rate law is probably the most comprehensive and largely used to interpret the kinetics of water–rock interaction. In the framework of this theory, Aagaard and Helgeson (1982) have established the following rate law for silicate reactions:

$$\frac{d\xi_m}{dt} = f_m s_m \sum_{i=1}^{i_{Tm}} k_{im} \left\{ \prod_{n=1}^{n_{Tm}} a_n^{-N_{nim}} \right\} \left(1 - \exp\left[\frac{A_m}{\sigma_{im} RT}\right] \right)$$

(1)

where the symbols ξ_m, f_m, s_m and A_m are respectively: the reaction progress variable of mineral m, the proportion of surface effectively reactive, the total surface area and the chemical affinity of mineral reaction. k_{im} and σ_{im} are the kinetic constant and the *stoichiometric factor* of mechanism i relative to global reaction. The catalyst and inhibitor term, $(\prod_{n=1}^{n_{Tm}} a_n^{-N_{nim}})$, represents the activity product of reactant species evolved in the activation reaction relative to mechanism i. N_{nim} is the power (partial order) of the n_{Tim} species reactant activity. i_{Tm} represents the number of parallel mechanisms involved in the global reaction of mineral m. R and T represent the gas constant and the absolute temperature. Although the transition state rate law (equation 1) is an explicit function of chemistry of the aqueous solution, it is difficult to evaluate all parameters incorporated in this law. Thus, equation (1) is usually simplifed to:

$$\frac{d\xi_m}{dt} = k_m S_m f_m a_{H^+} \left[1 - \exp\left(-\frac{A_m}{RT} \right) \right]$$

(2)

In this form, the catalyst and inhibitor term has a value of one and therefore, only the pH effect on reaction rate is considered via a_{H^+}.

Previous work

Recent experimental work on the dissolution reaction rate of albite (Oelkers *et al.*, 1993) have shown the necessity to consider the catalyst and inhibitor factor. Consequently, although transition state theory is based on well recognized principles, its application is not universally adopted. Morever, the interpretation of experimental results, using this theory, is not unique because of the difficulty in determining the catalyst and inhibitor factors as well as the effective area of the reactive mineral surfaces.

The kinetic constants (k_m) of global dissolution reaction of some aluminosilicates determined on the basis of expression (2) exist in the literature and are quoted (Azaroual, 1993). In fact, they are only apparent constants because they refer to the measured total surface of the mineral concerned.

The kinetic simulation of water-rock interaction requires accurate knowledge of reactant mineral surfaces. The geochemical reaction rates (in mol/cm²/s) were normalised to the area of the interface between mineral and aqueous solution. Unfortunately, it is very difficult to estimate this area parameter. In practice, two methods are used:

- the B.E.T. method using an inert gas such as N_2, Ar or Kr. Chow and Grant (1988) have shown that the use of Kr yields more precise and reproducible results than N_2. In contrast, Anbeek (1992) has advised using N_2 to estimate solid surfaces,

- the geometric method based on an assumed geometrical shape and arrangement of solid grains (spheres, cubes, ...). This approach systematically gives surface areas that are lower than those obtained with the B.E.T. method.

Furthermore, the mineral surface reactivity is a function of the free energy of the different crystalline sites and crystalline defects. During

TABLE 1. Kinetic characteristics (specific surfaces and kinetic constants of minerals at 180°C) used in this work

Minerals (K-20)	volume %	$S_m(cm^2/kg\ H_2O)$	f_m (%)	$k_m(180°C)$ $(mol/cm^2/s)$
Quartz	28.43	4.20 E+6	3.2	1.20 E–13
K-feldspar	19.57	2.82 E+6	0.32	1.00 E–13
Plagioclase: -albite -anorthite	40.35	5.90 E+6	0.32	4.78 E–13
Biotite : -annite -phlogopite	7.97	1.24 E+6	0.03	2.33 E–12
Hematite	0.92	2.70 E+5	0.03	1.00 E–14
Calcite	0.11	1.80 E+4	0.07	5.00 E–11

reaction, the reactive surface can increase if surface irregularity increases (etch pits development, tortuosity, etc ...) or decrease due to the coalescence of etch pits or as result of the complete dissolution of minerals.

Simulation of water–rock interaction

In our work, an experiment of interaction of a Soultz granite with distilled water was conducted at a temperature of 180°C and a pressure of 14 bar over 38 days (cf. Azaroual et al., 1994; this volume). We have attempted to model this experiment using the EQ3/6 geochemical software (Wolery, 1979).

The total surface area (table 1) was measured using N_2-B.E.T. method. The kinetic constants of dissolving minerals at 180°C were estimated from values at 25°C and activation enthalpy using the Arrhenius law. Equation (2) was used to compute the dissolution rate of primary minerals and the local equilibrium approach was adopted for homogeneous reactions and secondary precipitations (calcite, saponite, muscovite and chlorite).

The kinetic simulation is in agreement with the observed repartition of dissolutions and precipitations. SEM observations of primary minerals after experiment have allowed to estimate the relative proportion of the total measured (B.E.T.) surface area effectively reactive. These estimates were further refined by adjusting the values (f_m in table 1) that optimized internal consistency

(chemical composition of aqueous solution and secondary minerals; calcite, saponite, and probably chlorite and muscovite) with the experimental results. Values of f_m parameter comprised between 0.03 to 3 % (table 1) are obtained.

Conclusion

In first approximation, values comprised between 0.03 to 3 % (table 1) for the proportion of surface effectively reactive are obtained. These values are very low and may be specific to the system studied in our experiment.

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