Dissolution of Gibbsite in Open and Closed Systems: Experimental Data and a New Kinetic Approach

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Introduction

In sedimentary and diagenetic environments the decomposition and neoformation of solids is mostly related to the interaction between water and rock. Near the earth surface thermodynamic equilibrium is rarely reached. Thus the composition of the associated minerals, and of the liquids, e.g. surface, ground and interstitial waters, may change continuously as the reactions proceed. Interpretation of geochemical data and development of geochemical models require experimental data and basically kinetic approaches (e.g. Casey et al., 1993).

Assuming weathering reactions the specific ratios between water and rock has to be known. In natural surroundings these ratios are very different. In order to obtain dissolution rates at boundary conditions experiments have been carried out in mixed flow through reactors (open system) and batch reactors (closed system).

In a first step it is essential to investigate the interaction between aqueous solutions and individual minerals, preferentially solids with a simple composition and a widespread occurrence in natural systems. In the present study gibbsite is used which is a common mineral in soils, sediments, and sedimentary rocks and which may be a major constituent of sedimentary deposits, e.g. bauxite.

Experimentals

The dissolution experiments were carried out with well crystallised gibbsite ($2 <$ particle size $< 30 \mu m$; $0.6 m^2$ BET surface/g) in one litre solution and at a constant temperature in the range from 20 to $60 \pm 1°C$. The solution was kept at constant pH via the addition of hydrochloric, sulphuric, silicic, and citric acid.

The one litre PE batch reactor containing the suspension is permanently rotated at 25rpm. After various time periods samples were collected. In the mixed flow through reactor 240 ml suspension is continuously stirred. An input solution is pumped into the reactor at flow rates between 0.0006 and 0.4 l/h. Fractions of the output solution were sampled after passing a $0.1 \mu m$ filter.

Results and discussion

In principal the dissolution of gibbsite may be expressed by the reaction

$$k_1\ Al(OH)_3 + 3\ H^+ = Al^{3+} + 3\ H_2O\ (1)\ k_2$$
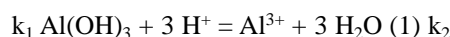
where k_1 ($l^3 m^{-2} h^{-1} mol^{-2}$) and k_1 ($l\ m^{-2} h^{-1}$) denote the rate constants of the dissolution and of the back reaction, respectively.

In a new approach the measured evolution of aluminium concentration is directly related to the individual values of the reaction rate constants k_1 and k_2. This approach is applied to both, experiments in open and in closed systems. Thus kinetics may be compared at the boundary conditions via the values of k_1 and k_2. Furthermore this permits to distinguish between the reaction rate of the dissolution and of the back reaction, respectively.

The results show that the values of the rate constants k_1 and k_2 are in the same order of magnitude for both sets of experiments, in open and closed systems. Therefore the present kinetic approach permits a mutual application of the rate constants within the boundary conditions for modelling natural environments.

In general aluminium concentration at equilibrium is higher with respect to sulphuric and citric acid versus hydrochloric and silicic acid. This may be due to complexation of Al^{3+} with the dissolved compounds in the solution.

A similar behaviour is obtained for the value of k_1. In analogy to the reactions in aqueous solutions this may be also related to a complexation of the dissolved components at the surface of gibbsite. Surface complexation increases significantly the dissolution rate of gibbsite. Moreover it is important to note that surface complexation affects the value of k_1 but rather not that of the back reaction k_2. Nevertheless the value of k_2 depends on temperature.

If these results are applied to the formerly used overall dissolution rates (R; e.g. Mogollon et al., 1996) it is shown that the dissolution rates $RG = k_1\ [H^+]^3$ of the present study are higher or equal (RG >= R). Thus the new kinetics approach permits to distinguish between dissolution and back reaction according to equation 1, where R represents the "dissolution plateau" of the overall dissolution of gibbsite.

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Mogollon JL, Ganor J, Soler JM, Lasaga AC, *Am.J.Sci.*, **296**, 729-765, (1996).