

Experimental study of kyanite dissolution rates as a function of Al and Si concentration

E.H. Oelkers
J. Schott

Laboratoire de Géochimie, CNRS-Université Paul Sabatier, 38
rue des Trente-six Ponts, 31400 Toulouse, France.

Introduction

The goal of this work is the comprehensive understanding of the variation of aluminosilicate dissolution/precipitation rates with saturation state as a function of crystal structure. The accurate characterization of this behaviour is essential for the successful application of rates measured in the laboratory at far from equilibrium conditions to the near to equilibrium conditions typical of natural processes. Following the application of transition state theory to quartz, aluminosilicate hydrolysis rates have been commonly been assumed to be independent of chemical affinity at far from equilibrium conditions. Over the few years, studies have been performed to assess the validity of this assumption for albite (Oelkers and Schott, 1992, 1994a), kaolinite (Devidal *et al.*, 1992, 1994; Devidal, 1994), K-feldspar (Gautier *et al.*, 1994) and anorthite (Oelkers and Schott, 1994b). These studies demonstrated that dissolution rates are not generally independent of chemical affinity at far from equilibrium conditions, but rather vary as simple function of aqueous aluminum and/or silica concentration. Building on these results, the present study was initiated to assess the variation of kyanite on chemical affinity, and the concentrations of aqueous aluminum and silica.

Experimental methods

Natural kyanite crystals having an average size of ~10 cm were obtained from Wards Natural Science. These crystals were hand picked, then ground with an agate mortar and pestle and sieved. The size fraction between 50 and 100 μm was cleaned ultrasonically using acetone to remove fine particles, rinsed with distilled water, and dried overnight at 80°C. By analogy with other minerals prepared by this method, the specific surface area of the cleaned powder was estimated to be 800 cm^2/gm . The chemical composition of the kyanite, determined by electron microprobe is given in Table 1.

Dissolution experiments were carried out in

TABLE 1. Elemental analysis of the kyanite used in the present study obtained from microprobe analysis

Element	Atom percent
Si	12.7
Al	24.5
Fe	0.25
O	62.5
Others	0.05

fluids comprised of demineralized/degassed H_2O , Merck reagent grade HCl , and AlCl_3 , and H_4SiO_4 obtained by the dissolution of amorphous silica for one week at 90°C. The input solution compositions were chosen so that they would have a $\text{pH}=2$ at 150°C. All experiments were carried out at a temperature of 150°C and $\text{pH}=2$ in a titanium mixed flow reactor system, as described in detail by Berger *et al.* (1994). This reactor system is ideally suited to investigate the reaction rates of water/mineral interaction, as the saturation state and composition of the fluid can be regulated by either changing the flow rate or the composition of the input solution without dismantling the reactor, and/or changing the amount of mineral present during the experiment. A steady state dissolution rate, as indicated by a constant output concentration of Al and Si, was obtained after an elapsed time ranging from 2 to 24 hours, depending on the flow rate. The silica and aluminum composition of the input and output fluids were determined using the molybdate blue method (Koroleff, 1976) and flameless atomic absorption in a graphite furnace (Perkin Elmer Zeeman 5000), respectively. The pH of the output fluids were measured immediately after sampling. In all cases the pH of the solutions was unchanged during the experiment.

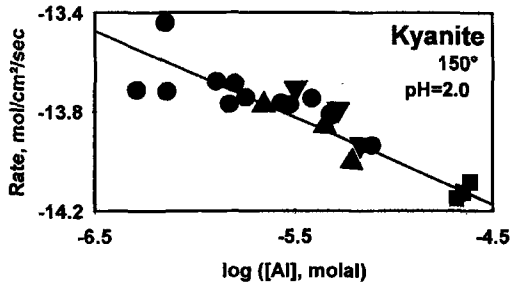


FIG. 1. Logarithm of kyanite dissolution rates as a function of the logarithm of total aluminum concentration. The symbols designate the composition of the input solution: circles: $[Al_i] = [Si_i] = 0$; inverted triangles $[Al_i] = 0$, $[Si_i] = 5$ ppm; upright triangles $[Al_i] = 0$, $[Si_i] = 1$ ppm; squares $[Al_i] = 0.5$ ppm, $[Si_i] = 0$ (see text).

Experimental results and discussion

Steady state dissolution rates (r) were computed from the measured solution compositions using

$$r = \frac{m_i F \Delta v_i}{s} \quad (1)$$

where Δm_i refers to the concentration difference between the input and output of the i th element in solution, F designated the fluid flow rate, represents the stoichiometric number of moles of the i th element in one mole of the kyanite, and s refers to the total mineral surface area present in the reactor. Logarithms of resulting steady state rates are depicted as a function of the logarithm of the total aluminum concentration in figure 1. The total aluminum and silica concentrations of these steady state experiments ranged from $5.0 \times 10^{-7} \text{ m} \leq [Al_{\text{total}}] \leq 2.5 \times 10^{-5} \text{ m}$, and $2.5 \times 10^{-7} \text{ m} \leq [Si_{\text{total}}] \leq 1.8 \times 10^{-4} \text{ m}$. These solute concentrations are undersaturated with respect to all mineral phases, and no secondary phases were apparent on the kyanite sample following the experiments. All experimental results exhibited stoichiometric dissolution. Taking account of thermodynamic properties computed from SUPCRT92 (Johnson *et al.*, 1992) and solute activities calculated with EQ3NR (Wolery, 1983), these solute concentrations correspond to chemical affinities ranging from ~ 60 to ~ 100 kJ/mol. The distribution of data in Fig. 1 indicates that far from equilibrium kyanite dissolution rates

are independent of aqueous silica concentration, but decrease with increasing aqueous aluminum concentration. The line drawn through the data in Fig. 1 is consistent with

$$r = k[Al_{\text{total}}]^{-1/3} \quad (2)$$

where k designates a rate constant. This same dependence of dissolution rate on aluminum at far from equilibrium conditions was found for albite (Oelkers and Schott, 1992, 1994a) and K-feldspar (Gautier *et al.*, 1994). Such dependence results in the appearance that these dissolution rates are dependent on chemical affinity at far from equilibrium conditions, and implies that the dissolution of kyanite is controlled by an aluminum deficient precursor complex (Schott and Oelkers, 1993; Oelkers *et al.*, 1994).

References

- Berger, G., Cadore, E., Schott, J. and Dove, P. (1994) *Geochim. Cosmochim. Acta*, **58**, 541–52.
- Devidal, J.-L. (1994) PhD. Thesis, University of Toulouse 3.
- Devidal, J.-L., Dandurand, J.L. and Schott, J. (1992) In *Water Rock Interaction*, (Kharaka, Y.K. and Maest, A.S. eds.) A.A. Balkema: Rotterdam, **1**, 93–6.
- Devidal, J.-L., Dandurand, J.L. and Schott, J. (1994) (in preparation).
- Gautier, J.-M., Oelkers, E. H. and Schott, J. (1994) *Geochim. Cosmochim. Acta*, (submitted).
- Johnson, J. W., Oelkers, E. H. and Helgeson, H. C. (1992) *Computers and Geosci.*, **18**, 899–947.
- Koroleff, F. (1976) In: K. Grasshoff (Editor), *Methods of Seawater Analysis*. Springer Verlag, New York, 149–58.
- Oelkers, E.H. and Schott, J. (1992) *Geol. Soc. Amer.*, (Abstract with programs), **24**, A–207.
- Oelkers, E. H., Schott, J. and Devidal, J.L. (1994) *Geochim. Cosmochim. Acta*, (in press).
- Oelkers, E. H. and Schott, J. (1994a) (in preparation).
- Oelkers, E. H. and Schott, J. (1994b) (in preparation).
- Schott, J. and Oelkers, E. H. (1993) In: M. Cuney and M. Cathelineau (Eds) *Proceedings of the 4th International symposium on Hydrothermal Reactions*. Institut Lorrain des Sciences, Nancy, 221–6.
- Wolery, T.J. (1983) UCRL-53414. Lawrence Livermore National Laboratory, Livermore, CA.