

## An experimental study of quartz precipitation and dissolution rates at 200°C

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The understanding and quantification of quartz-water interactions is essential for modelling mass transfer in crustal fluids. Quartz dissolution kinetics at hydrothermal temperatures have been the subject of many investigations. Recently, Berger *et al.* (1994) used a mixed flow reactor to produce data over a wide range of solution compositions, which enabled an improved understanding of the quartz dissolution mechanism. Much less work has been performed on quartz precipitation, and in particular the effect on the rates of changing solution composition. Rimstidt and Barnes (1980) and Bird and Boon (1985) used a closed system technique to generate rate constants from their data, but to date no direct quartz precipitation rate measurements have been performed. In this study direct measurements of quartz dissolution/precipitation rates were made as a function of solution saturation state at the near equilibrium conditions typical of natural processes.

Experiments were performed at 200°C using a titanium mixed flow reactor system described by Berger *et al.* (1994). These reactor systems are ideally suited to investigate the rates of water/mineral interactions at both near and far from equilibrium conditions (Gautier *et al.*, 1994). Mixed flow reactors afford numerous advantages over closed system reactors for kinetic studies including 1) allowing direct measurement of steady-state rates, and 2) permitting rate measurements at specific fluid compositions by either changing the inlet solution composition or the fluid flow rate. The same natural quartz crystals were used in both dissolution and precipitation experiments. The crystals were ground and sieved to the 50–125 micron size fraction. Fine particles were removed by ultrasonic cleaning in deionized water. To remove remaining fine particles and the disturbed surface layer produced by grinding, the quartz grains were cleaned in a mixed flow reactor for five days at 250°C with deionized water. The B.E.T. specific surface area measured after the cleaning procedure was  $0.098 \pm 0.005 \text{ m}^2/\text{g}$ . The aqueous silica-rich inlet solutions used for precipita-

tion experiments were prepared by concentrating deionized water originally equilibrated with silicic acid at 90°C.

When starting a precipitation run, the reactor was filled with deionized water and heated to 200°C. Silica-rich solution was then pumped through the reactor. This procedure avoided any potential precipitation of non-quartz silica phases on the quartz grains that could occur from supersaturated solutions at temperatures less than 200°C.

To assess the possible effect of silica precipitation on the reactor walls and tubing, a blank test was made by pumping a silica-rich solution through the reactor containing no quartz sample. Only a slight decrease of the outlet silica concentration, less than one percent of the inlet concentration, was observed.

Dissolution rates were measured at 200°C in atmosphere equilibrated deionized water (pH of 5.65 at 25°C). Steady-state outlet silica concentrations ranged from  $4.13 \times 10^{-5}$  to  $2.70 \times 10^{-3} \text{ m}$ . Each of the dissolution data points shown in Fig. 1 corresponds to an individual run conducted at a specific flow rate. Quartz solubility was measured at 200°C in a  $5 \times 10^{-4} \text{ m}$  NaOH solution using the same solid as used for the kinetic study but of a smaller size fraction (40–60 microns). The measured solubility of  $4.55 \times 10^{-3} \text{ m}$  of Si corresponds to a calculated quartz dissociation constant at 200°C of  $4.27 \times 10^{-3}$ .

Precipitation experiments were performed using inlet fluids containing from 145 to 253 mg/kg of Si and at flow rates ranging from 0.01 to 0.18 ml/min. Steady-state outlet concentrations ranged from 141 to 198 mg/kg of Si. The B.E.T. specific surface area measured after the last experiment was  $0.0745 \pm 0.005 \text{ m}^2/\text{g}$ , which is slightly lower than the original measurement.

Dissolution rates exhibit a linear dependance on the saturation state consistent with rate laws derived from the Transition State Theory and the principle of detailed balancing (Lasaga, 1981) given by:

$$R = k_r(1 - Q/K), \quad (1)$$

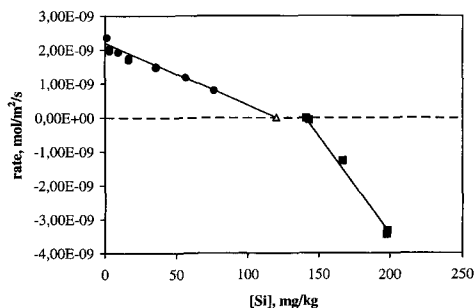


FIG. 1. Quartz dissolution and precipitation rates as a function of steady-state silica concentration at 200°C. The filled circles and squares correspond to dissolution and precipitation rates, respectively, whereas the solid lines represent fits of these data - see text.

where  $k_+$  designates the dissolution rate constant,  $Q$  stands for  $H_4SiO_4$  concentration and  $K$  represents the quartz dissociation constant. Regression of the data obtained in the present study yields values of  $2.2 \times 10^{-9}$  mol/m<sup>2</sup>/s and  $4.27 \times 10^{-3}$  for  $k_+$  and  $K$  respectively. The rate constant is in good agreement with that reported by Tester *et al.* (1994). The value of  $K$  derived from quartz dissolution experiments is equal to that directly measured in a closed reactor system and compares well with the literature data. Precipitation rates measured in this study can be fit with Eqn. 1, but with values of  $8.0 \times 10^{-9}$  mol/m<sup>2</sup>/s and  $4.98 \times 10^{-3}$  for  $k_-$  and  $K$  respectively. Moreover, experiments performed on quartz grains following

their use in precipitation experiments indicate an initially enhanced dissolution rate compared to the original fresh quartz sample.

Rimstidt and Barnes (1981) showed that the values of  $k_+$  and  $K$  for the different silica polymorphs follow the order: amorphous silica > cristobalite > quartz. Thus, it would be reasonable to attribute the high values of  $k_+$  and  $K$  to the poor crystallinity of the hydrothermally precipitated quartz. It should be noted, however, that the growth of cristobalite or amorphous silica on the starting grains was thermodynamically unfavoured as all reacting solutions contained less than 200 mg/kg of Si. Moreover, Rimstidt and Barnes (1981) established that the precipitation constant  $k_- = k_+/K$  should be the same for all silica polymorphs, but in this study, the value of  $k_-$  is three times greater for precipitation than for dissolution.

## References

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