

Kinetics and mechanisms of dissolution of silica at room temperature and pressure

S. Plettinck
L. Chou
R. Wollast

Laboratoire d'Océanographie Chimique, Université Libre de
Bruxelles, Campus de la Plaine - C.P. 208, B-1050 Brussels,
Belgium

Introduction

Numerous studies have been conducted recently concerning the dissolution kinetics and mechanism of quartz or amorphous silica at various temperatures ranging from 25 to 300°C (see Dove and Elston, 1992 and Berger *et al.*, 1994 for reviews). These investigations have been mainly concentrated on the influence of pH and of electrolyte solutions on the dissolution rate, and various mechanisms have then been proposed, mostly in terms of surface complexation models. Although these studies have contributed to a better understanding of the reaction mechanism, there still remain questions which need to be addressed and clarified regarding mainly the existence of a minimum in the rate of dissolution of quartz as a function of pH and on the nature of surface complexation sites and their quantification.

We have therefore studied the rate of dissolution of amorphous silica and quartz at close pH intervals especially at low pH's. The influence of concentrations of various cations (Li, Na, K, Cs, Mg, Sr and Ba), anions (Br, Cl, SO₄ and NO₃) and organic acids (acetic, citric and oxalic acids) have also been investigated in detail so that their effects on the rate can be better quantified.

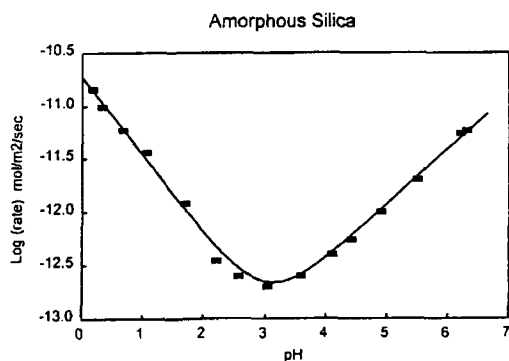


FIG. 1. Log rate of dissolution as a function of pH.

Methods

High purity amorphous silica powder for chromatographic purpose (Belgolabo) was used in all experiments without any pretreatment. Quartz crystals from Brazil were first crushed coarsely with an iron crusher and then ground with an iron mortar. Fractions less than 63µm were collected and ultrasonically cleaned with 1 N HCl and then 1N NaOH to eliminate fine particles (less than 1µm). Pretreated quartz powder was washed abundantly with distilled-deionized water before use.

All our experiments were conducted in batch reactors at room temperature and pressure under well controlled conditions with only one parameter varying at one time. Solid/solution ratio was maintained constant: 2.5 g/l for amorphous silica and 20 g/l for quartz. Dissolved silica was analyzed colorimetrically following the method described in Grasshoff *et al.* (1983). All standards were prepared in solutions which was used in the experiments to avoid interference from salts present.

Results and discussion

The existence of a rate minimum at pH close to 3 has been clearly established and the rate dependence of pH on both sides of the minimum well defined. Figure 1 shows the rate of dissolution of amorphous silica as a function of pH for values 6. The dissolution rate expressed in terms of mol m⁻²sec⁻¹ can be described by the following equation:

$$r = 10^{10.73} a_{H^+}^{0.74} + 10^{-14.51} a_{H^+}^{-0.52}$$

The enhancement of the rate of dissolution by NaCl can be explained by the formation of Na surface complexes. The concentration of these complexes can be described by a simple Langmuir isotherm (see Figure 2) and the rate of dissolution at a fixed pH of 6.3 can be expressed by:

$$r = \frac{1.9 \times 10^{-11} m_{NaCl}}{0.3 + m_{NaCl}} + 0.58 \times 10^{-11}$$

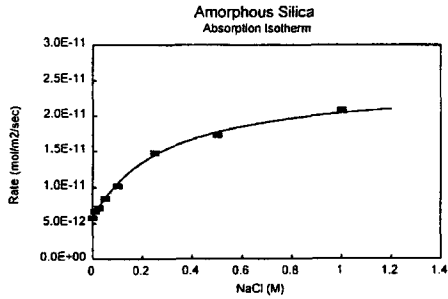


FIG. 2. Rate of dissolution as a function of NaCl at pH 6.3

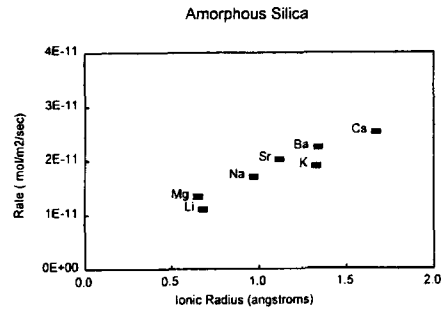


FIG. 3. Rate of dissolution as a function of ionic radius of cations investigated.

where the constant term represents the rate of dissolution in the absence of Na^+ .

The order of rate increase for the cations considered in chloride solutions is $\text{CsCl} > \text{BaCl}_2 > \text{SrCl}_2 > \text{KCl} > \text{NaCl} > \text{MgCl}_2 > \text{LiCl}$. The concentrations of the salt solutions were 0.5 M at pH 6.3. This order of rate increase shows a good correlation with the ionic radius of the individual ion in question (Figure 3). For the same cation studied, only a small effect of the various anions investigated on the dissolution rate was observed, suggesting that it was the nature of cations involved in the dissolution step which controls the rate. Various models of the distribution of

complexation sites involving protons and cations and their effect on the rate of dissolution have been tested and compared to models previously presented in the literature.

References

- Berger G., Cadore E. Schott J. and Dove P.M. (1994) *Geochim. Cosmochim. Acta* **58**, 541–51.
- Dove P.M. and Elston S.F. (1992) *Geochim. Cosmochim. Acta*, **56**, 4147–56.
- Grasshoff K., Ehrhardt M. and Kremling K. Editors (1983) *Methods of Seawater Analysis*. Verlag Chemie, Weinheim, 2nd Edition, 419 p.