



# Dissolution kinetics of quartz in water at high temperatures across the critical state of water



Ronghua Zhang\*, Xuotong Zhang, Shumin Hu

Laboratory of Geochemical Kinetics, MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Baiwanzhuang Road 26, 100037 Beijing, China

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## ABSTRACT

The steady-state dissolution kinetics of quartz in water has been measured at temperatures from 20 to 435 °C at pressures of 23 and 33 MPa using a continuous stirred-tank reactor. Dissolution rates were found to increase with increasing temperature from 20 to 374 °C at 23 MPa, giving an Arrhenius expression of  $\log k_+ = -1.6478 - 13,573.1/T(K)$ , but then decreased on further increasing the temperature beyond 374 °C. At 33 MPa, the rates increased with temperature up to 400 °C, giving an Arrhenius expression of  $\log k_+ = -1.325 - 14,124/T(K)$ , but then decreased on further increasing the temperature. At a constant temperature below 350 °C, quartz dissolution rates were found to increase with increasing pressure. At around the critical state of water, the dissolution rates fluctuated as a result of sharp changes in the properties of the medium (e.g., density, dielectric constant, ionic product).

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## 1. Introduction

Measurements of quartz dissolution rates have been pursued in numerous laboratories for more than 50 years. Investigators have sought to gain a thorough understanding of the mechanism of hydrothermal reactions between silicate minerals and water in the Earth's crust and at deeper locations, or to quantify dissolution rates for various chemical processes (e.g., synthesis, processing) over a wide range of temperatures [1–21].

Results have generally confirmed that the dissolution kinetics of oxide and silicate minerals is dependent upon the formation of surface complexes, the interaction of solute reactants with these surface complexes [15,20–22], the compositions of reactant solutions [5,7,9,16–18,20–22], and how far the system is from the equilibrium state [5–9,11–18,23–33]. Since the 1990s, investigators have found that alkali metal cations strongly influence the dissolution rates of quartz at temperatures  $\leq 300$  °C [16–24,33–36]. The present investigation focuses on the effects of the properties of water on the dissolution behavior of quartz as conditions are varied around the critical region of water.

Quartz/water interface chemical processes have been observed and examined by means of SEM, HRTEM, and AFM [27]. As reported

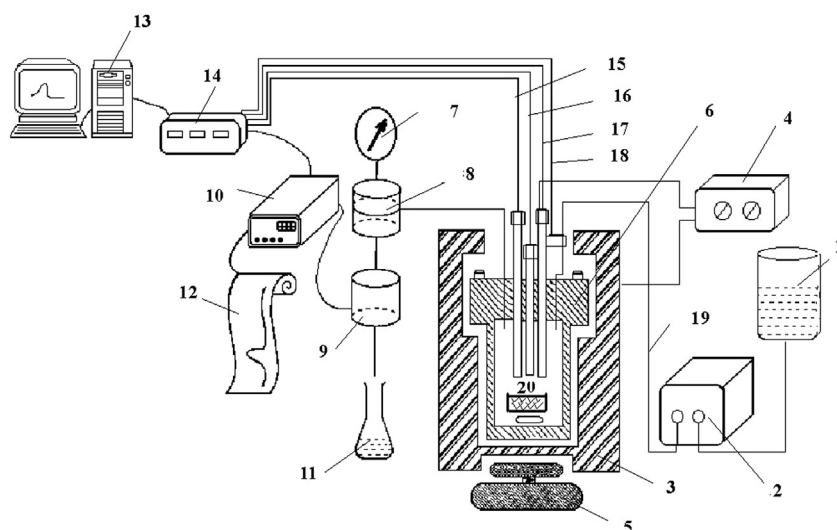
by many investigators [20,36,37], three different types of surface complexes can appear on quartz: singly ( $-\text{Si}(\text{OH})_3$ ), doubly ( $=\text{Si}(\text{OH})_2$ ), and triply ( $\equiv\text{SiOH}$ )-linked Si tetrahedral units. It was found that as three or two highly polarized bonds are formed at the surface, respectively, the dissolution rates of singly- and doubly-coordinated complexes are distinctly higher than in the case of triply-linked silicon tetrahedral complexes [20]. Many investigations have indicated that quartz dissolution rates vary strongly with the pH of the reactant solution. The strong pH dependence of the dissolution rate is attributed to changes in the surface speciation of quartz [12,26,38–42].

Many investigators have suggested that dissolution rates exhibit a linear dependence on the saturation state, consistent with rate laws derived from transition state theory and the principle of detailed balancing given by [6,16,22,34,43]:

$$R = k_+ \left( 1 - \frac{Q}{K} \right) \quad (1)$$

where  $k_+$  denotes the dissolution rate constant,  $Q$  denotes the  $\text{H}_4\text{SiO}_4$  activity, and  $K$  represents the quartz dissociation constant. In other words, researchers have found that silicate dissolution rates appear to depend on how far from equilibrium the system is [16,22,34,44]. Here, the  $1 - Q/K$  term represents the displacement of the reaction from equilibrium, such that  $Q/K$  is the saturation index. The rate is not strictly linear with respect to  $1 - Q/K$ , in particular at relatively close to equilibrium.

\* Corresponding author. Tel.: +86 10 68326411; fax: +86 10 68326995.  
E-mail address: [zrhsm@pku.edu.cn](mailto:zrhsm@pku.edu.cn) (R. Zhang).



**Fig. 1.** Schematic illustration of the mixed flow reactor used in this study. 1, water reservoir; 2, liquid pump; 3, furnace; 4, temperature controller; 5, magnetic stirrer; 6, titanium vessel; 7, pressure gauge; 8, back pressure regulator; 9, electric conductivity detector; 10, detector; 11, sampling bottom; 12, recording; 13, computer and monitor; 14, electricity meter; 15–18; electro-chemical sensors; 19, tubing; 20, sample box of titanium network.

Among mineral dissolution experiments, to the best of our knowledge only one investigation has focused on the effect of pressure on quartz dissolution rates [45]. Typically, quartz dissolution rates have been measured over a wide temperature range from 25 to 300 °C [1–26,28–35,46,47]. Only a few experiments on mineral dissolution kinetics have been performed at temperatures above 300 °C and pressures above 22 MPa [2–4,6,11,15,22]. Consequently, our understanding of the hydrothermal processes that occur at higher temperatures (>374 °C) and pressures is incomplete.

Previous solubility experiments on quartz have been performed at temperatures up to 800 °C [48–53]. Recently, the solubility of quartz in aqueous fluids and fluid mixtures has been extensively studied from ambient conditions up to 1100 °C and 200 MPa [54,55]. However, the results obtained at equilibrium conditions cannot be used to adequately interpret the kinetic mechanisms of the reactions of water with silicate under non-equilibrium conditions at temperatures above 300 °C and pressures above 23 MPa.

Previous experiments and theoretical studies have indicated that anomalies in the properties of water are associated with fluctuations in parameters such as density, dielectric constant, ionic product, or others (e.g., compressibility, diffusivity, and viscosity) that diverge at its critical point [56–58]. Hence, these variations in the properties of water at temperatures above 300 °C affect silicate dissolution kinetics therein from the subcritical to the supercritical state.

In this study, experiments on quartz dissolution kinetics have been performed using a continuous stirred-tank reactor (CSTR) at temperatures from 20 to 435 °C and at pressures of 23 and 33 MPa. The purpose of these experiments is to provide new insight into the quartz dissolution mechanism in water from the subcritical state to the supercritical state.

## 2. Experimental

### 2.1. Apparatus

Quartz dissolution experiments were carried out using a continuous stirred-tank reactor (CSTR) in the temperature range from 25 to 435 °C at 23 and 33 MPa. The experimental apparatus consisted of a titanium vessel, a liquid pump, a back-pressure regulator, a furnace, a temperature controller, temperature and pressure sensors, an electrical conductivity detector, and a computer for data

acquisition and monitoring (see Fig. 1). The vessel used in our experiments had an inner length of 10 cm, an inner diameter of 5 cm, and a total volume of 196 mL. CSTRs have previously been used to perform kinetic experiments on mineral dissolution [16,22,59–64].

### 2.2. Experimental procedure

The large-crystal quartz used in the experiments was natural quartz supplied by the Beijing Geological Museum. It was collected from a quartz-vein-type of gold deposit in Hunan province, China. Mineral particles were crushed in a shatter box and sieved to 20–40 mesh. Pure quartz particles were then identified and hand-picked by observation under an optical microscope (at 50× magnification). The pure quartz particles were again crushed in a shatter box and sieved to 20–120 mesh. The quartz particles thus obtained were cleaned ultrasonically using acetone to remove fine particles, rinsed with distilled water, and dried at 70–80 °C.

Typically, 5 g of quartz crystals was placed in a box made of titanium mesh inside of the vessel. Water was continuously introduced into the vessel from the bottom at different flow rates, and passed through the quartz particles. The water is de-ionized and degassed water (dd water). After the reaction, the effluent from the vessel was passed through an electronic conductivity detector (Orion star A212, Thermo Scientific). Before sampling, on-line monitoring of changes in the conductivity of the effluent throughout the experiments showed the point at which dissolution of the mineral reached a steady state.

At the start of each new run, the CSTR was conditioned with flowing water (dd water) at room temperature for 1–2 days to help reduce any high-energy surfaces and to remove very fine particles adsorbed on the surface [63,64]. When starting a new run (i.e., after 1–2 days), we took effluent samples at hourly intervals at a constant flow rate, constant temperature, and constant pressure.

A series of experiments was performed, systematically varying the temperature and flow rate. If the flow rate was changed under conditions of constant input medium (i.e., dd water), temperature, and pressure, the system attained a new steady state after 1 h or more. We then took samples of the effluent at regular intervals in order to determine the dissolution rate. The experimental equipment and method have been described previously [61–65].

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