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# Precipitation of Silica Minerals by Hydrothermal Flow-Through Experiments at 200-430 °C and 30 MPa

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## Keywords

*Quartz precipitation, hydrothermal flow-through experiments, quartz vein, silica polymorph*

## ABSTRACT

Hydrothermal flow-through experiments were conducted to understand the kinetics and mechanism of precipitation of silica minerals from Si-saturated aqueous solutions. The Si-saturated solutions were created by dissolution of silica glass at 350 °C. The first series of runs consisted of precipitation experiments using 31 grams of quartz sand (grain size of 1-2 mm) at 200-430 °C and 30 MPa with flow rate of 0.5 g/min. The decrease in Si concentration during the pass through the quartz sand was less than 50 ppm at temperatures below 350 °C, whereas the Si concentration after pass-through at 430 °C reaches close to equilibrium solubility. This indicates that temperatures of > 400 °C are suitable for observing the precipitation of a substantial amount of silica minerals at 30 MPa within several days, because of the low equilibrium solubility and the high reaction rate. The second series of runs consisted of the precipitation experiments (430 °C, 30 MPa) from a supersaturated solution ( $C_{Si} = 638$  ppm) with using granite substrates with a flow rate of 0.7-1.0 g/min for 80 hours. The total amount of precipitated silica minerals was 3.4 g, and the amount decreased with increasing distance from inlet, indicating that Si concentration of the solution decreased during the pass through the reaction tube. The precipitated silica minerals and textures varied along the flow path. Near the inlet, Opal C was precipitated on the surface of the stainless tube. At 14-20 cm from the inlet, quartz overgrew on quartz grains within the granite substrate, but fine-grained quartz crystals (10-100  $\mu\text{m}$ ) were deposited on other minerals and on the stainless tube. At 20-30 cm from the inlet, quartz precipitation was restricted to the pre-existing quartz surfaces of the granite. Our results suggest that nucleation and formation of  $\text{SiO}_2$  polymorphs other than quartz were important for the formation of the quartz veins under high degree of supersaturation ( $C/C_{eq} > 2$ ), whereas precipitation sites within the crack was substantially controlled by mineral species

within the crack wall under low supersaturated conditions. This suggests that the internal crystal growth textures of vein minerals provide constraints on the fluid compositions within flow paths.

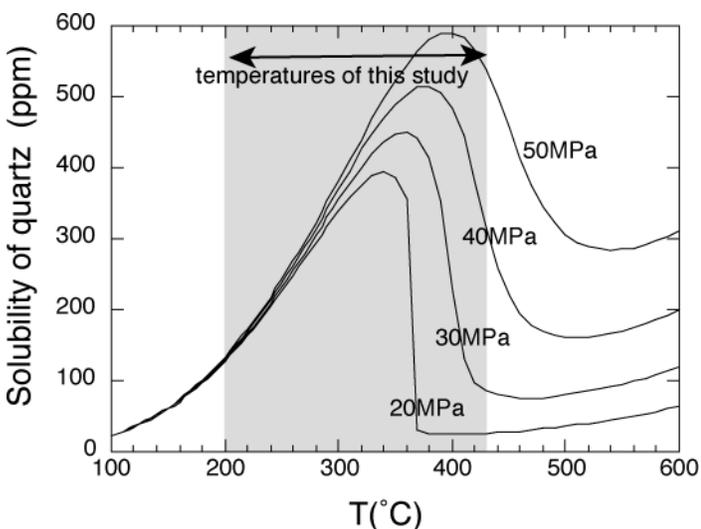
## Introduction

Silica scale is one of the practical problems experienced in the operation of geothermal power plants. In natural systems, mineral veins composed of quartz commonly occur in the Earth's crust under various geological settings including ore mineralization, fault systems, accretionary complex and metamorphic rocks (e.g., Okamoto et al., 2008). Thus, an understanding of kinetics and textural development during the precipitation of quartz and other silica polymorphs are important to evaluate hydrology and material transport under crustal conditions. Also, dissolution and precipitation behavior of silica minerals in laboratory experiments can give useful and fundamental information for understanding the formation of silica scale in artificial facilities such as pipelines and boreholes in geothermal systems.

Precipitation of silica minerals and the formation of quartz veins commonly occur at temperatures around or below brittle/ductile transitions ( $T = \sim 400$  °C). Even monomineralic quartz veins contain a variety of crystal growth textures (e.g., Bons, 2000). The primary texture of quartz veins is essentially controlled by the relative rates of nucleation and growth, and the crystallization sites. Recently, several studies have described development of vein texture based on flow-through experiments of polycrystal growth of calcite (Lee et al., 1996; Lee and Morse, 1999), and Alum (Hilgers and Urai, 2002; Hilgers et al., 2004; Nollet et al., 2006) at room temperatures (< 50 °C). These studies show that (1) crystals grow on mineral grains of the same composition within the substrate, (2) the growth rate decreases from the inlet to the outlet corresponding to the decrease in solution concentrations by precipitation, and (3) growth competition occurred among adjacent crystals with different crystallographic orientations. Although these studies provide many implications to the formation of natural quartz veins, there are still several uncertainties. First, quartz veins forms within various kinds of host rocks (igneous, sedimentary, and metamorphic rocks) composed of not only quartz

but also other silicate minerals, and thus it is important to know which mineral surfaces are available for quartz crystallization. Second, ubiquitous occurrence of blocky veins suggests that certain conditions favor nucleation in fluids rather than crystal growth from walls. Also, there are several silica polymorphs other than quartz. These factors are essential to constrain progressive evolution of permeability of fractures during sealing within various kinds of lithology.

In the present study, we conducted hydrothermal flow-through experiments to understand kinetics and textural development of quartz precipitation from silica-saturated solutions at conditions of 200–430 °C and 30 MPa. The experimental conditions lie over the boundary between liquid and supercritical phases of water. Quartz solubility reaches its maximum around 350–400 °C at pressures of < 100 MPa, and it drastically decreases with increasing temperature due to the increase of specific volume of water (Fournier and Potter, 1982; Tsuchiya and Hirano, 2007; Figure 1). Tsuchiya et al. (2007) have investigated water-granite interaction by hydrothermal flow-through experiments with a temperature gradient. They found that substantial quartz precipitation occurred at temperatures higher than 400 °C for several days.

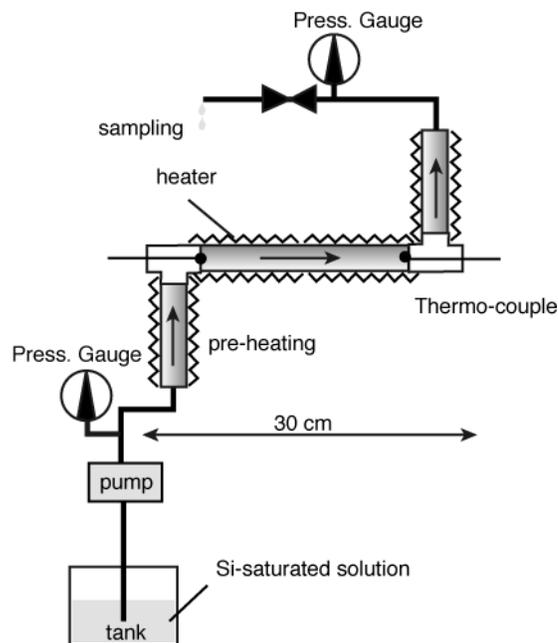


**Figure 1.** Quartz solubility for the experimental conditions (200–430 °C, 30 MPa) of this study (Fournier and Potter 1982).

We carried out two series of precipitation experiments using (1) quartz sand, and (2) granite substrate. In the first experiments, we evaluated the effect of temperature on the precipitation rate of silica minerals. In the second experiments, the precipitation textures of silica minerals were observed as well as the effects of the degree of supersaturation and precipitation sites on the precipitation mechanism of silica minerals.

## Experimental Design

The apparatus consisted of stainless tubes of 500 mm with an internal diameter of 10.5 mm, and the quartz sand or granite substrate were set at positions of 14–35 cm from the inlet. Samples of the solution from the outlet of the reaction tube were weighted, treated with a 0.2 μm filter, diluted with water to a Si



**Figure 2.** Experimental apparatus of the flow-through experiments of this study.

concentration less than 100 ppm and then stored in polyethylene containers until they could be analyzed. The concentration of silica was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) at Tohoku University.

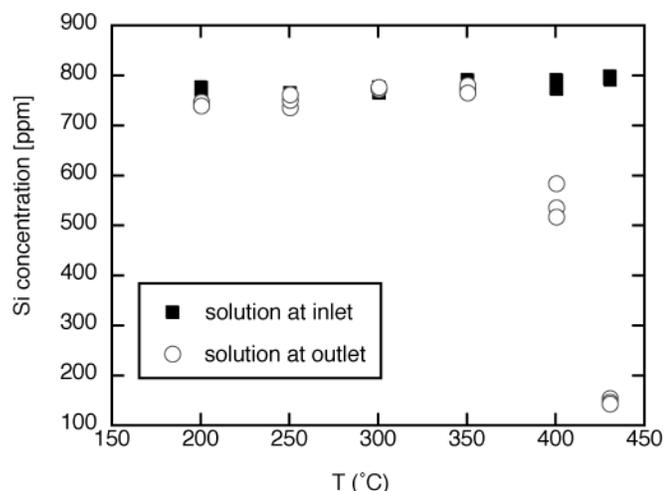
For the first experiments, we used quartz sand of nearly homogeneous grain size (1–2 mm). The flow rate was 0.5 g/min, and thus the resident time decreases from 306 minutes for 200 °C to 4.9 minutes for 430 °C. The specific area of this sand was 0.007–0.008 m<sup>2</sup>/g (the average of four measurements was 0.00725 m<sup>2</sup>/g), determined by argon BET. Quartz sand with a mass of 31 g was packed in the tube, and a silica-saturated solution flowed through this porous medium. This silica-saturated solution (750–800 ppm) was created by dissolution of silica glass at 350 °C.

In second experiments, 6 rectangular granite substrates (6.5 x 6.5 x 30 mm) were set within the reaction tube along the lateral flow path. The pressure-temperature (P-T) condition of the precipitation is 30 MPa and 430 °C, and the flow rate is 0.7–1.0 g/min. The Si concentration of the initial solution was 638 ppm. The solutions after precipitation was sampled, and measured by ICP-AES. The precipitated materials were observed by using SEM and optical microscopy and were identified by X-ray diffractometer (XRD).

## Results and Discussion

### Temperature Dependency of Silica Minerals

Figure 3 shows the Si concentration of the solutions before and after passing through quartz sand. The decrease in Si concentration was less than 50 ppm at temperatures below 350 °C. On the other hand, the changes in Si concentration was ~ 200 ppm at 400 °C, and ~ 600 ppm at 430 °C, indicating the precipitation of silica minerals. At 430 °C, the Si concentration after pass-through ( $C_{Si}$ ) was 142–154 ppm. The precipitation rate constant,  $k_p$ , is



**Figure 3.** Si concentrations of initial solutions and of solutions after passing through the reaction tube with quartz sand at temperatures of 200 – 430 °C.

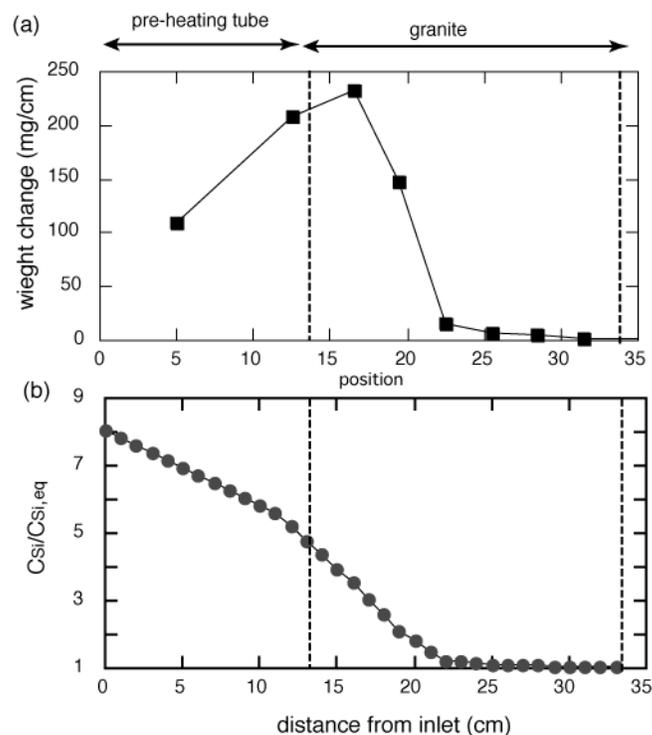
calculated from the Si concentrations,  $C_{Si}$ , as follows (Rimstidt and Barnes, 1980):

$$k_t = -(M/A) \ln [(1-S)/(1-S^0)] / t, \quad (1)$$

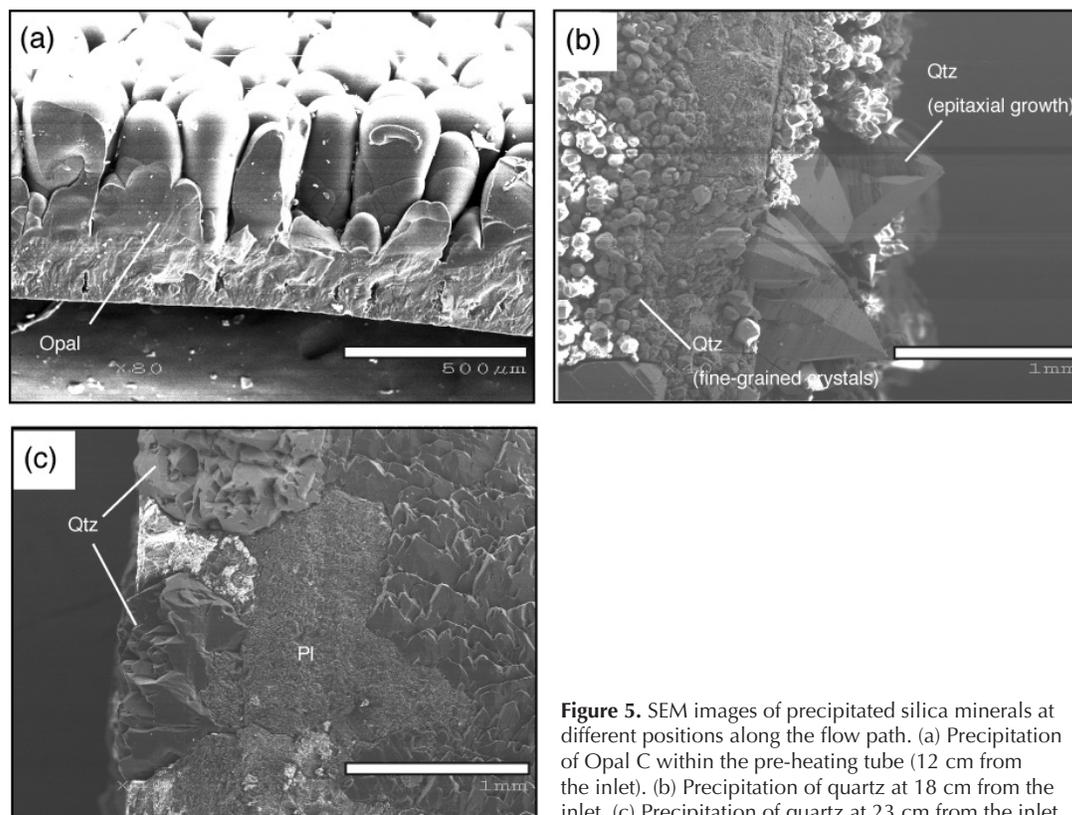
where  $S$  and  $S^0$  is degree of supersaturation of silica ( $= C_{Si}/C_{Si,eq}$ ) for the initial solution and the solution after time  $t$ , respectively.  $A$  and  $M$  indicate the relative reactive surface area and relative mass of the water, respectively. The precipitation rate constants at 400 and 430 °C are  $2.2 \times 10^{-5}$  and  $9.6 \times 10^{-5}$  [ $s^{-1}$ ], respectively. These values are consistent with the previous studies that carried out below 350 °C (Rimstidt and Barnes 1980; Bird et al. 1986). The results of this study indicate that experimental temperatures above 400 °C are suitable for the observation of precipitation textures, because a large amount of silica precipitation ( $> 1$  g) occurs for several days

### Precipitation of Silica Minerals

During the second experiment, the Si concentration at the outlet was constantly about 90 ppm. Figure 4a shows the weight change of granite substrate. The silica precipitated not only on the granite substrate, but also within the pre-heating tube (0-14 cm from the inlet). The amount of precipitated silica was large near inlet, and it drastically decreased toward the outlet. Assuming that the precipitation rate was constant through the experiment, the change in Si concentration



**Figure 4.** (a) Weight changes of granite substrate (30 mm long) after the precipitation experiments for 80 hours. Positive values indicate the precipitation of silica minerals. (b) Si-concentration of solutions with respect to the distance from inlet. The Si-concentrations were calculated by using Si-concentrations at inlet and outlet, and the precipitation amounts of silica minerals along the flow path.



**Figure 5.** SEM images of precipitated silica minerals at different positions along the flow path. (a) Precipitation of Opal C within the pre-heating tube (12 cm from the inlet). (b) Precipitation of quartz at 18 cm from the inlet. (c) Precipitation of quartz at 23 cm from the inlet.

along the flow path can be calculated from the Si concentrations of inlet and outlet and the amount of precipitated silica (Figure 4b). The degree of supersaturation ( $S = C_{Si}/C_{Si,eq}$ ) was initially 8, and it decreased to 4 at 15 cm from the inlet, and it was below 1.5 at 22 cm. Incongruent dissolution of K-feldspar and plagioclase of granite substrates were observed from the solution compositions as observed by Hara and Tsuchiya (2005), but the concentrations of dissolved K and Ca ions were less than 1 ppm.

The materials and textures of precipitation of silica minerals changed with increasing distance from the inlet. Within the pre-heating tube (0-15 cm from the inlet), silica precipitation occurred on the surface of stainless tube and the precipitated material was Opal C (Figure 5a). At positions of 14-20 cm from the inlet, the precipitated material was quartz, but the precipitation textures differed among the precipitation sites (Figure 5b). On quartz surfaces of the granite substrates, quartz overgrew with the same crystallographic orientation of substrate quartz crystals. On the other hand, on feldspars of granite substrates or on stainless steel tube, fine-grained euhedral quartz crystals (10-100  $\mu\text{m}$ ) were deposited. At positions of 20-30 cm from the inlet, quartz grew on the quartz grains, but no precipitation occurred on the minerals other than quartz.

In natural veins, growth from the crack wall (elongate-blocky texture) and nucleation and growth in fluids (blocky texture) could occur at similar P-T conditions (Okamoto et al. 2008). Our results imply that the formation of blocky veins (nucleation within fluids) will occur for high Si-saturated solutions ( $S > \sim 2.0$ ) via the formation of amorphous silica or cristobalite, whereas elongate-blocky or fibrous veins (growth on pre-existing minerals) were formed under low degree of supersaturation ( $S < \sim 2.0$ ). In addition, cracks would be sealed homogeneously under high-supersaturation without the effect of wall rock, whereas precipitation of quartz would be substantially controlled by wall-rock types under low supersaturation. Thus, the crystal growth pattern within the vein provides useful information on solution compositions passing through fractures under crustal conditions.

## Acknowledgements

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