MINERALOGICAL VARIATION OF SILICA INDUCED BY AL AND NA IN HYDROTHERMAL SOLUTIONS

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ABSTRACT

Various silica minerals form in hydrothermal settings; however, the main controls on mineralogical variations in such environments remain poorly understood. In this study, we investigate the effects of Al and Na on the mineralogy of silica precipitates by hydrothermal flow-through experiments for silica precipitation at 430 °C and 31 MPa. We used solutions with elevated Si concentrations, exceeding the solubility of amorphous silica. As the Al and Na concentrations in the input solution were raised from 0 to 7 ppm, the dominant silica minerals systematically changed from amorphous silica to cristobalite to quartz. The positive correlation between Al and Na contents in precipitated quartz indicates that Al coupled with Na substitutes for Si. Our results suggest a possible mechanism for quartz vein formation in which quartz nucleates directly without precursor amorphous silica or cristobalite due to the presence of feldspar-derived Al and Na in hydrothermal fluids.

Keywords: Hydrothermal experiments, silica precipitation, quartz, amorphous silica, trace elements, feldspar

INTRODUCTION

Silica is one of the dominant constituents of the Earth’s crust, and its dissolution–precipitation behavior has a marked effect on the crust’s hydrological and mechanical properties (e.g., Sibson 1992). While quartz is the most stable phase of silica, various metastable polymorphs commonly occur in surface and subsurface silica deposits, including amorphous silica (opal-A), cristobalite (opal-C/CT), and chalcedony. The solubilities and dissolution/precipitation rates of individual silica minerals have been extensively investigated (e.g., Rimstidt and Barnes 1980; Akinfiev and Diamond 2009). Mineralogical variations in silica deposits are generally considered to result from nucleation of amorphous silica, followed by transformation to higher-ordered phases (e.g., Steefel and Van Cappellen 1990), and have been used as an indicator of relative age of deposits (e.g., Herdianita et al. 2000). Quartz grains in hydrothermal veins do not always grow from preexisting quartz grains on vein walls, but some veins are filled by equant quartz grains (blocky texture; e.g., Okamoto and Tsuchiya 2009); however, in contrast to surface silica deposits, hydrothermal quartz veins do not contain the relics of other silica polymorphs (e.g., Rusk and Reed 2002). Accordingly, it is unclear whether these quartz grains were transformed from amorphous silica or not. Hydrothermal quartz veins contain various trace elements, including Al, Ti, Li, and Na (e.g., Monecke et al. 2002). Okamoto et al. (2010) found that the mineralogy of the silica precipitates from solutions that interacted with granite differed from those from solutions that interacted only with quartz.

In the present study, we synthesized silica minerals in hydrothermal flow-through experiments. We show a systematic change in the mineralogy of silica deposits with the concentrations of Al and Na in the solutions, and discuss the formation of hydrothermal quartz veins influenced by trace elements in the Earth’s crusts.

EXPERIMENTAL METHODS

The experimental apparatus consisted of three cylindrical stainless steel reaction vessels of various lengths (diameter, 10.1 mm) connected in series to create a horizontal flow path (Appendix Fig. 1). The fluid pressure and the flow rate were maintained at 31 ± 1 MPa and 2.0 ± 0.5 g/min, respectively. For preparing the input solution, distilled water flowed into the first vessel to dissolve albite [Na/(Na+Ca+K) = 0.99] at varying temperatures (160–330 °C) and then in the second vessel (length, 25 cm) to dissolve quartz at 360 ± 1 °C. The Al and Na concentrations were controlled by the temperature of the first vessel. In this study, the temperature measurements were accurate to approximately 1 °C. Silica was precipitated in the third vessel (length, 51 cm) at 430 ± 1 °C, because the solubility of quartz decreases with increasing temperature from 360 to 430 °C at 31 MPa (Akinfiev and Diamond 2009). At 430 °C and 31 MPa, the solubilities of amorphous silica (Si,eq,AS), cristobalite (Si,eq,X), and quartz (Si,eq,Q) are 220, 176, and 77 ppm (which is equivalent to mg/kg solvent), respectively (Okamoto et al. 2010; Akinfiev and Diamond 2009). In the precipitation vessel, we did not use any rock/mineral substrates.

During individual runs, the input and output solutions (i.e., before and after passing through the precipitation vessel, respectively) were periodically sampled after quenching. The concentrations of Si, Al, and Na in the solutions were determined using an inductively coupled plasma–atomic emission spectrometer (ICP–AES; Thermo-Scientific iCAP 6300 Duo View, Tohoku University, Japan). The pH of the solutions was measured at room temperature (25 °C). After each run, the products collected from the precipitation vessel were dried at 90 °C for 24 h, weighed, and identified using an X-ray diffractometer (XRD; Rigaku MIniFlex II, Tohoku University, Japan). The chemical compositions of the products were determined using an electron probe microanalyzer (EPMA; JEOL 8200, The University of Tokyo, Japan).

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