Water Rock Interaction [WRI 14]

Disturbance of thermodynamic equilibrium of the quartz-water system and silica separation from the liquid phase at a small temperature gradient

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Abstract

In electric furnaces destined for experimental geochemical investigations, a small temperature gradient (TG) always exists, and it is difficult to avoid it. In our electric furnaces (from bottom to top) the temperature rises in the lower part (TG = 0.25 °C/cm) and falls in the upper part (TG = -0.16 °C/cm). Long-term runs with quartz and water at 300°C have shown the attainment of equilibrium at TG equal to -0.16 °C/cm. At TG equal to 0.25 °C/cm, the silica re-precipitated from the ampoule bottom onto its walls above the meniscus, and the aqueous silica concentration was reduced and became 300 times lower than quartz solubility. The obtained results were explained by the combined action of slow convection of water and thermal diffusion of silica. The efficient mechanism of fractionation revealed by us can be extended to other substances and has geochemical and technological importance.

Keywords: quartz; water; silica; disturbance of equilibrium; temperature gradient; thermal diffusion; slow convection; separation

1. Introduction

In previous paper [1], we have revealed in some long-term runs at 300°C the transformation of thermodynamic equilibrium quartz-water system into non-equilibrium one whereas in other runs such transformation was not observed. Some hypotheses were proposed to explain this unusual silica behavior and estimations of their reliability were made. In this study, we present results of new experiments on this subject and give a new explanation of the results taking into account different Temperature Gradients (TG) in the upper and lower parts of electric furnaces.

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2. Methods

Crushed natural quartz with the grain size of 10-63 μm and distilled water (the Quartz/Water mass ratio was 0.005) were placed into Au or Pt ampoule. The ampoule was hermetically sealed and heated in autoclave at 300°C. Two series of runs were fulfilled: 1) quartz + water in Au ampoules at $K = 0.68$ ($K$ was the filling of ampoules with water at run temperature) and 2) quartz + water + Pt net in Pt ampoules at $K = 0.53$ (the net was situated vertically so that the meniscus at run temperature was at the middle of the net). The autoclaves were heated coupled, one on another, in aluminum block situated in the middle of the vertical electric furnace. The values of TG in the Al block were 0.25 and –0.16 °/cm at the levels of lower and upper autoclave respectively. Positive and negative signs of the TG mean that the rise and decrease of the temperature from below to up prevents water from mixing and promotes its mixing respectively at the expense of buoyancy forces. After the given time at 300°C, autoclaves were quenched in cold water and ampoules were open. Solutions were filtered (the pore size was 0.05 μm) and analyzed for silica concentration (ICP-AES and photometry). The disposition of secondary silica phases was determined using endoscope. Then these phases were scraped and analyzed using X-ray diffraction, scanning electron microscopy, and BET method (for measurements of specific area).

3. Results

In experiments fulfilled in upper autoclaves, the aqueous silica concentration ($m$) was not changed with time and was equal to quartz solubility (Fig. 1). Initial quartz in these experiments was always retained on the ampoule bottom and new solid phases were not formed. These data show the achievement of thermodynamic equilibrium in quartz-water system.

In experiments fulfilled in lower autoclaves, the following stages of the process can be outlined (Fig. 1 and Table 1): 1) initial quartz was still presented ($m = 7-8$ mmol/kg), 2) initial quartz was completely transformed into microcrystalline opal-C or opal-CT ($m = 1-2$ mmol/kg), and 3) the opal was completely transformed into secondary quartz ($m = 0.03$ mmol/kg). The new minerals were formed on ampoule walls considerably above the meniscus at run temperature at the very top of the ampoule or at the upper edge of Pt net. The both new minerals had high specific area ($s$) (Table 1) owing to small crystal size of opal or small numerous pores in quartz crystals (Fig. 2).

![Fig. 1. Aqueous silica concentration ($m$) vs time ($t$) in the series quartz + water (a), and quartz + water + Pt net (b). Runs were conducted in upper autoclaves (empty symbols) with $TG = -0.16$ °/cm and in lower autoclaves (filled symbols) with $TG = 0.25$ °/cm. Dashed lines show quartz solubility in water at 300°C [2]. Vertical solid lines show stage boundaries for the process in lower autoclaves.](image-url)
4. Discussion

Integrity of ampoules was controlled by the equality of silica masses in them before and after the runs and also by the absence of silica in the water between outer ampoule walls and inner autoclave walls. The absence of silica precipitation from solution during quenching was proved by special experiments with high ratio of $A/M$ ($A$ is the surface area of quartz, $M$ is the water mass) close to $A/M$ values in our runs (Table 1). In these experiments fulfilled in upper autoclaves under the same conditions, values of $m$ in quenched solution were equal to quartz solubility in water at 300ºС. Thus unusual silica behavior in lower autoclaves was a consequence of not methodical mistakes but small positive value of TG.

Under conditions of our experiments, quartz is a stable mineral [3]. It has the lowest solubility in water among all silica modifications, which are unstable and transform into quartz with time [4]. The results of our runs fulfilled in lower autoclaves show disturbance of quartz-water equilibrium and silica localization

![SEM-photo of microcrystalline opal (a) and porous crystals of secondary quartz (b) formed on ampoule walls above the meniscus.](image-url)

**Table 1. Results of long-term experiments carried out in the lower part of electric furnace (TG = 0.25 °/cm).**

| $t$ (days) | $m$ (mmol/kg) | New minerals | $s$ (m$^2$/g) | $A/M$ (m$^2$/kg) |
|-----------|---------------|--------------|---------------|-----------------|
| Series quartz + water |
| 410       | 0.60          | opal-CT      | 109           | 545             |
| 591       | 2.58          | opal-CT      | 95            | 475             |
| 775       | 1.01          | opal-CT      | 190           | 950             |
| Series quartz + water + Pt net |
| 84        | 2.38          | opal-C       | 260           | 1300            |
| 261       | 2.27          | opal-C       | 310           | 1550            |
| 441       | 5.66          | opal-C + quartz | 120     | 600             |
| 533       | 0.031         | quartz       | 114           | 570             |
| 625       | 0.029         | quartz       | 78            | 390             |
in the upper part of ampoules. This contradiction is explained by more duration of our runs. Silica separation proceeds slower than silica dissolution or precipitation and so the separation was not revealed earlier in experiments with considerably shorter duration. Positive TG is the initial reason of silica separation but we want to know mechanism of this process. In previous paper [1], we proposed that this mechanism was the predominant evaporation of water at the meniscus edge [5].

Now we suppose that a more probable mechanism can be thermal diffusion (Soret effect) providing additional silica flux upwards owing to temperature gradient [6]. In efficiency of separation, our experimental cell resembles thermogravitational column using not only thermal diffusion but also convection. One way to increase separation is to slow down the convection by inclination of the column [7]. The separation can be increased also in thermal diffusion cell by its inclination or creation of horizontal TG [8]. In our lower autoclaves, ampoules were inclined and probably they were under the conditions of not only vertical but also horizontal TG. This caused water convection but with much slower rate than in upper autoclaves, i.e. the rate ratio of thermal diffusion and convection might be close to optimal for maximal separation. In vapor phase with quartz solubility of 3 ppm at 300°C [9], convection and thermal diffusion can take place also. Both these processes in liquid and vapor phases can interact with each other through their common boundary surface.

Owing to common character of the proposed mechanism, the separation can be displayed with not only silica but with other matters. Thus knowledge of TG may be important for all reactions in experiments. Geochemical application of the work is that the role of thermal diffusion in concentration of elements may be considerably larger than it was considered till now if thermal diffusion of solution components takes place together with slow convection of solutions. This peculiarity can be used also with technological aims for effective separation of matters.

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