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Transformation of equilibrium quartz-water system into non-equilibrium one under a small temperature gradient

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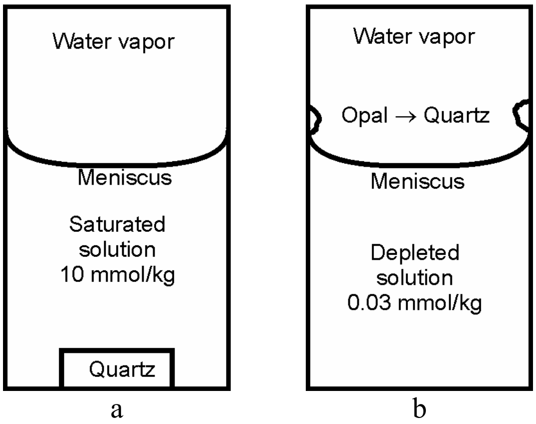


Fig. 1. Schematic image of the state of quartz-water system in ampoules: a – equilibrium state (<100 days), b – non-equilibrium state (>600 days).

Introduction. In previous experiments with quartz-water system at 300ºC [*Alekseyev et al.*, 2006; 2007; *Alekseyev and Medvedeva*, 2009], we have obtained the following results. At the initial period, quartz situated at the bottom of ampoules was partially dissolved forming saturated solution (Fig. 1a). As quartz is stable silica mineral under these conditions [*Dove*, 1995], this state is considered to be equilibrium and it can be maintained theoretically for an infinitely long time. However after ~100 days, the following changes were started (Fig. 1b). At the meniscus edge on the ampoule wall, metastable opal was formed and later it was transformed into secondary quartz. Primary quartz at the ampoule bottom was completely dissolved and water was completely depleted with silica. As a result, all silica was moved from ampoule bottom and from the solution onto the ampoule walls above the meniscus. The task of this work was 1) specification of the conditions under which this paradoxical behavior of silica displays, 2) determination of the depletion limit of solution with silica, and 3) search and evaluation of the hypotheses explaining the experimental data.

Methods of the experiments were the same as they were earlier [*Alekseyev et al.,* 2006; 2007; *Alekseyev and Medvedeva*, 2009]. Crushed natural quartz (10-63 μ) cleaned from ultra fine particles [*Alekseyev et al.,* 2010] and distilled water with mass ratio Q/W = 0.005 were placed into Au or Pt ampoule, welded up hermetically, and heated in autoclave at 300ºC. The chosen Q/W ratio provided more than eight-fold excess of silica with respect to quartz solubility at 300ºC. The part of water filling the ampoule ($K_{\text{fil.}}$) at 300ºC was 0.68 (series A) and 0.53 (series B). The ampoules were heated in autoclaves with water ($K_{\text{fil.}}$ = 0.68 at 300ºC) to create the pressure of saturated water vapor necessary to compensate the inner vapor pressure (to prevent ampoule break) at run temperature.

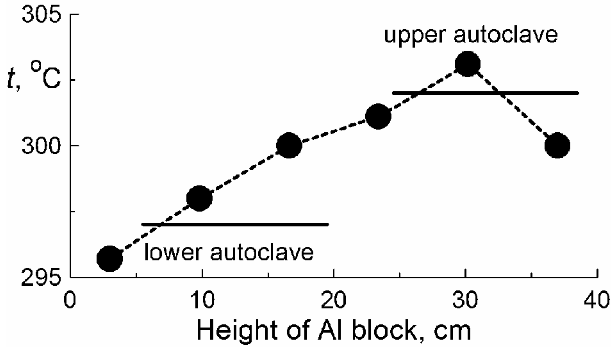
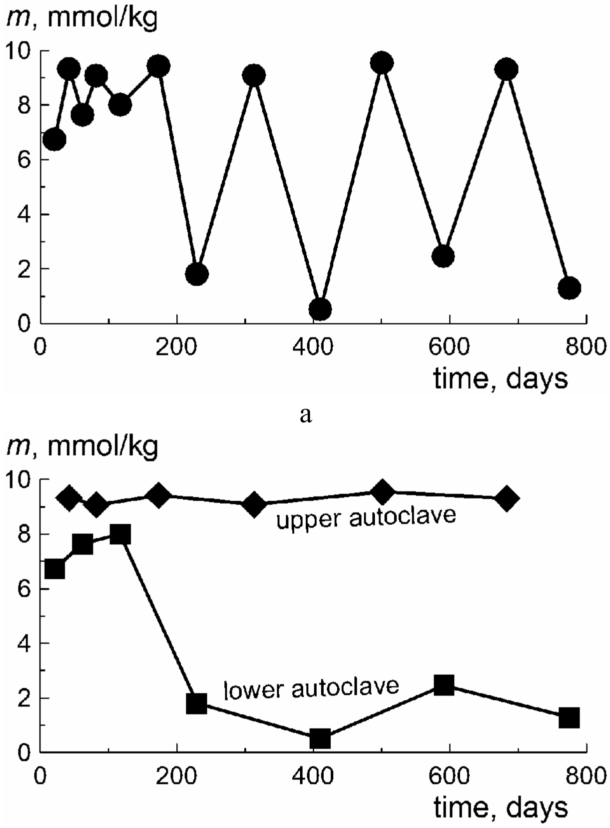


Fig. 2. Temperature distribution along the height of Al block situated in the electric furnace. The horizontal lines show the positions of autoclaves.

For heat, autoclaves were placed in pairs, one on top of the other, into the holes of Al block situated in electrical furnace. At the site of the lower autoclave disposition, the temperature of Al block rises from bottom to top with gradient 0.25 º/cm (Fig. 2). Such temperature distribution relative to gravitation force is stable as it prevent water mixing at the expense of buoyancy force. In the ampoule of the lower autoclave therefore, one can expect the same temperature gradient as in the Al block. At the site of the upper autoclave disposition, the temperature of Al block first increases and then decreases from bottom to top (Fig. 2). In the ampoule of the upper autoclave, such temperature distribution is unstable as buoyancy force must lead to water mixing in ampoule, i.e. to temperature equalization. As a result, the temperature gradient in the ampoule of the upper autoclave must be close to 0.

After exposure at 300°C for a given time, autoclaves were quickly (during 20 s) quenched in cold water, ampoules were opened, solutions were filtered (pore size was 0.05 µ), diluted with HCl (2 %), and silica concentration was determined using ICP-AES and photometry with accuracy of 5 relative %.



a

b

Fig. 3. Aqueous silica concentration (*m*) vs. time in quartz-water system at 300°C. Series A: $K_{\text{fil.}}$ = 0.68. a – total data, b – the data were grouped depending on temperature gradient: ~0 (upper autoclave) and 0.25 °/cm (lower autoclave).

Experimental results in series A are characterized, like earlier [*Alekseyev et al.*, 2006; 2007; *Alekseyev and Medvedeva*, 2009], by large data scattering (Fig. 3a). This scattering however has regular alternation of high and low concentrations caused by alternation of upper and lower autoclave drawing out. In the runs fulfilled in the upper autoclaves (temperature gradient is ~0), aqueous silica concentration corresponds to quartz solubility [*Rimstidt and Barnes*, 1980] and in the runs fulfilled in the lower autoclaves (temperature gradient is 0.25 °/cm) aqueous silica concentration is lower and it decreases with time (Fig. 3b). Similar picture was in series B (Fig. 4). The difference was that in the last two runs of series B aqueous silica concentration was very low: 0.029 and 0.027 mmol/kg, i.e. it was more than 300 times lower than quartz solubility. The same value (0.027 mmol/kg) we obtained earlier [*Alekseyev and Medvedeva*, 2009] that makes one to assume the attainment of the limit of depleted solution.

Observation of the ampoule inner walls using endoscope has shown that the secondary silica precipitates onto ampoule walls only in the lower autoclaves. Two sites of precipitation predominates: 1) at once above the meniscus at 300°C (series B) and 2) at the extreme ampoule top (series A).

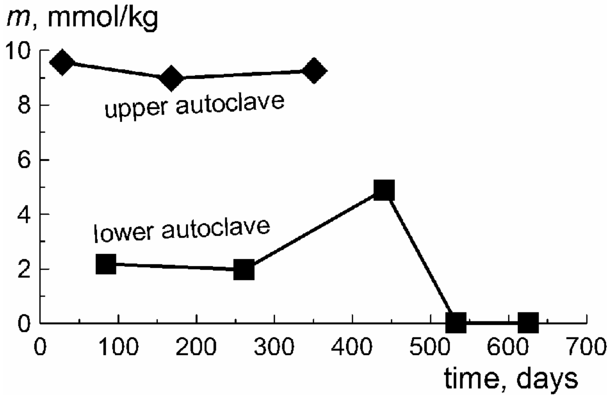


Fig. 4. Aqueous silica concentration (*m*) vs. time in quartz-water system at 300°C. Series B: $K_{\text{fil.}}$ = 0.53. The data were grouped depending on temperature gradient: ~0 (upper autoclave) and 0.25 °/cm (lower autoclave).

Discussion. Some hypotheses explaining experimental results will be examined below.

Disruption of ampoule insulation can lead to moving of the part of dissolved silica from the ampoule into the autoclave and as a result to the lowering of aqueous silica concentration in the ampoule. Our measurements have shown however that silica masses before and after the runs are equal in the ampoules. Only in one run of series B, the ampoule was not hermetic and this was clear determined by the ampoule mass change (this run was rejected).

Quenching effect can be realized in silica precipitation during quenching as a result of the decrease in quartz solubility with the decrease in temperature. Our calculations using rate equation of quartz precipitation [Rimstidt and Barnes, 1980] have shown the following. Aqueous silica concentration can decrease noticeably (>5 relative percents, i.e. more analytical error) if the ratio of S/M (S is mineral surface area, M is water mass) will be greater than 10^7 m^2/kg. In our runs, this ratio is certainly lower than 500 m^2/kg.

Simple recrystallization under temperature gradient proceeds through quartz dissolution in hot zone and its precipitation in cold zone. If temperature difference between the zones is small (as we have), the difference in quartz solubility in these zones is small (within analytical error). In our runs, quite different picture was observed. The secondary quartz was precipitated in hotter zone and aqueous silica concentration was hundreds times lower.

Formation of new mineral with low solubility is also impossible as all the secondary solid phases are well known and determined reliably using X-ray diffraction, infra red spectroscopy, and Raman spectroscopy [*Alekseyev et al.,* 2006; 2007; *Alekseyev and Medvedeva*, 2009]. They are stable quartz and metastable opal (with higher solubility). The features of the presence of other minerals were not revealed. The secondary quartz from the run with low aqueous silica concentration (0.027 mmol/kg) was dissolved repeatedly during shot period (one week) and gave high SiO_2 concentration (4.7 mmol/kg) [*Alekseyev and Medvedeva*, 2009]. It follows from this that low SiO_2 concentration at the presence of secondary quartz is explained by not its low solubility but its position above the water.

Solubility lowering in the pores of small size was estimated experimentally using Ostwald-Freundlich equation [*Mizele et al.,* 1985]. In the pores with minimal radius of 10 nm, amorphous silica solubility was 54 % of usual one. This effect displays in atmosphere with humidity < 100 %. In our runs different conditions were: 1) aqueous silica concentration was hundreds times lower than quartz solubility, 2) humidity was 100 %, and 3) only opal could be porous but not quartz crystals that only were presented at the latest stage.

Predominant evaporation at the meniscus edge can be real reason explaining our experimental data. In the extended meniscus being object of intensive study recently [*DasGupta et al.,* 1993; *Kim and Wayner*, 1996; *Panchamgam et al.,* 2008; *Sefiane and Ward*, 2007], three regions are separated: 1) adsorption film, 2) transition region (from contact line to the thickness of ~100 nm), and 3) bulk meniscus. In these studies, the profile of meniscus thickness was measured and then it was used in the Kelvin-Clapeyron model to obtain the profiles of temperature, pressure, heat and evaporation fluxes, liquid flow rate. Capillary force, disjoining pressure, and Marangoni stress were taken into account in this model. As a result, it was established that the transition region was characterized by the maximum of evaporation flux increasing when the wall temperature in the region of adsorption film was higher than in the bulk meniscus region [*DasGupta et al*., 1993], i.e. as in our lower autoclaves. Predominant evaporation in the transition region leads to the local temperature lowering resulting in the local increase of surface tension [*Panchamgam et al*., 2008]. As a result, the constant gradient of surface tension (Marangoni pressure) arises forming stable liquid flow from the bulk meniscus to the transition region. In the lower autoclaves, temperature increases from bottom to top intensifying this process to such extent that the flow rate of the liquid to the meniscus edge exceeds the diffusion rate of aqueous silica in the opposite direction. As a result, water evaporation at the meniscus edge leads to silica precipitation even in the case when the water in the bulk is undersaturated with respect to quartz. In reality, we have here transformation of equilibrium system into non-equilibrium one under the action of surface forces caused by small temperature gradient. Detailed and reliable examination of the stated hypothesis is connected with considerable difficulties as it demands elaboration of the methods measuring at high temperatures meniscus thickness and disjoining pressure of polar liquids. After this, calculations [*Panchamgam et al*., 2008] are necessary to carry out with adding equations of diffusion and precipitation rate of silica.

Thermal diffusion (Soret effect in liquids) can give additional silica flux from bottom to up at the expense of temperature gradient. When silica concentration in water vapor exceeds equilibrium concentration at the expense of this flux, silica precipitates onto ampoule walls. By this, in particular, it is explained the fact that the secondary silica was found not only at the meniscus edge but also at the ampoule top. Thermal diffusion is one of the methods of isotope separation. If our results are explained by thermal diffusion, separation of stable isotopes ^{28}Si, ^{29}Si, and ^{30}Si must be between water and secondary silica. This can be checked by isotopic analyses of silica in quenched solutions.

Conclusion. It was established experimentally that equilibrium quartz-water system transforms into non-equilibrium one under the temperature gradient of 0.25 °/cm (temperature rises from bottom to up). This is expressed in quartz redeposition from the ampoule bottom to the ampoule walls above the meniscus and in lowering of aqueous silica concentration from 10 to 0.03 mmol/kg. The experimental results cannot be explained by disruption of ampoule insulation, quenching effect, simple recrystallization, formation of new mineral with low solubility, or by solubility lowering in the pores of small size. Two hypotheses were proposed to explain unusual behavior of silica in the experiments: 1) predominant evaporation at the meniscus edge and 2) thermal diffusion. In both hypotheses quartz can be replaced by other mineral with preservation of the same consequences. The described phenomenon therefore can have general significance as it apparently can be revealed in experimental, technological, and natural systems of various composition.

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