

VIOLATING EQUILIBRIUM IN QUARTZ-WATER-VAPOUR SYSTEM

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Quartz (low quartz is implied here) is the most widespread silica mineral stable at least up to 573°C and 20 kbars [1, 2]. Opal is metastable silica mineral and transforms into quartz under natural and experimental conditions [3-9]. At temperatures near 300°C and pressure of water-vapour equilibrium (P_{SAT}), the duration of the above-mentioned experiments did not exceed a month. We conducted longer experiments in quartz-water-vapour system at 300-350°C and revealed that quartz within its stability field was transformed into opal [10, 11]. These results contradict to all published experimental data. Now we fulfilled considerably longer experiments under the same conditions. In this paper, the results of these experiments and also the hypothesis explaining them were presented.

Natural transparent quartz was used in experiments both as separate crystals and crushed materials with grain size of 10-60 μm . Two series of runs were performed using various mass ratios of the quartz and doubly distilled water: 1) 0.3-0.5 (a single quartz crystal) and 2) 0.0012 (crushed quartz). The experiments were performed in hermetically sealed gold or platinum ampoules at vertical position. At run temperature ($300 \pm 2^\circ C$), a vapour phase occupied about 30 % of ampoule volume minus quartz volume. After a given run duration, autoclaves were quenched in cold water. Solutions were filtered and analyzed for Si using inductively coupled plasma atomic emission spectroscopy. Inner walls of the ampoules were examined by endoscope to reveal the place of formation of new silica crusts. For more complete extraction of the crusts, a plastic scraper was used. The solid silica phases were washed, dried, weighted, and analyzed using a light microscope. Then they were crushed in corundum mortar and analyzed using X-ray powder diffraction.

Initial quartz was retained in all experiments of series 1 but aqueous silica concentration (m_{SiO_2}) was close to quartz solubility only in three experiments (Fig.). In two of them with duration of 146 and 297 days, mass loss of the quartz crystal was almost equal to the silica mass in solution and new silica phase was not observed (Table, series 1). In the rest experiments, m_{SiO_2} was lower than quartz solubility. In these two runs (250 and 383 days) and also in one experiment with m_{SiO_2} close to quartz solubility (235 days) mass loss of the quartz crystal was far in excess of the silica mass in solution (Table, series 1). In the same experiments, new-formed silica crusts were collected from ampoule inner walls in amounts correlated with mass loss of the crystal. The crusts were localized just above the solution meniscus in the form of distinct white rims comprised of glass bud-like material. They were identified by X-ray diffraction as opal-CT (235 days) and opal-C + quartz (250 and 383 days). Quartz in these samples had crystal size up to 2 mm and was secondary relative to the initial quartz crystal.

In the second series, initial quartz was retained only in two experiments with m_{SiO_2} close to quartz solubility (fig.). In the rest experiments of this series, m_{SiO_2} was considerably lower than quartz solubility and decreased with time to almost zero. In these runs, initial quartz was completely transformed

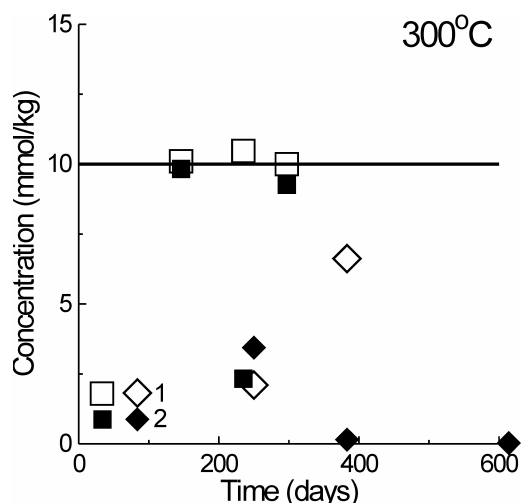


Fig. Concentration of dissolved silica versus time in quartz-water closed system at 300°C in the presence of water-vapour interface. 1 – series with quartz crystals (large excess of silica relative to quartz solubility); 2 – series with crushed quartz (two-fold excess of silica). The runs were performed in gold (squares) and platinum ampoules (rhombus). Horizontal line corresponds to quartz solubility [12].

Table

Conditions and results of the runs									
Duration (d)*	single quartz crystal (series 1)						crushed quartz (series 2)		
	Water mass (g)	Initial crystal mass (mg)	m_{SiO_2} (mmol/kg)	Mass loss of crystal (mg)	Silica mass in solution (mg) [†]	New silica phases (mg)	Water mass (g)	Initial quartz mass (mg)	m_{SiO_2} (mmol/kg)
146	1.43	483.45	10.1	0.80	0.87	<0.1	1.52	1.83	9.83
235	1.42	567.20	10.5	6.00	0.89	2.2	1.52	1.83	2.33
250	1.85	788.80	2.10	30.65	0.23	28.2	2.05	2.46	3.44
297	1.44	463.95	10.0	0.75	0.86	<0.1	1.52	1.83	9.26
383	1.86	883.70	6.62	89.6	0.74	85.4	2.125	2.55	0.15
614			Leakage				2.25	2.70	0.027

* The runs with duration of 146, 235, and 297 days were performed in gold ampoules. The rest of the runs were performed in platinum ampoules.

[†] Calculated from m_{SiO_2} and water mass.

into new silica phase. A thin white coating on inner ampoule walls above the meniscus represented this phase. We failed to collect it in amounts sufficient to identify using X-ray powder diffraction. Pleasant exception was the longest run with very low m_{SiO_2} equal to 0.027 mmol/kg (tab. series 2). In this run, a new silica phase was represented by a druse of crystals grown together above the meniscus in amounts equal to initial quartz mass (2.7 mg). It was identified as quartz only. This quartz was repeatedly dissolved in water at 300°C. As a result, m_{SiO_2} reached one-half the quartz solubility (4.8 mmol/kg) in a week already. This implies that here we are dealing with ordinary quartz and its ordinary solubility. Thus initial and final mineral in the reaction was the same. The distinction was that at the beginning of the reaction quartz was in the solution saturated with silica but at the end of the reaction quartz was above the solution depleted of silica.

We proposed the following hypothesis to explain mechanisms of this unusual reaction. In a closed quartz-water-vapour system, two dynamic equilibria are to be established with equal rates of oppositely directed processes: 1) chemical (dissolution and precipitation of quartz) and 2) physical (evaporation and condensation of water). During evaporation, only pure water converts into vapour and silica remains in solution. However, these equilibria are disturbed owing to a film transfer of the solution above the meniscus under the influence of surface forces [13]. Evaporation of the water leads to a more dramatic increase in m_{SiO_2} in the film than in the bulk of solution because of a small thickness of the film. Diffusion of aqueous silica from the film into the bulk of solution initiated by the concentration gradient is suppressed by the oppositely directed process of wetting ampoule walls with fresh portions of solution. As a result, usual opal precipitates above the meniscus. Silica is better wetted with water than gold or platinum [14]. Therefore formation of opal enhances movement and evaporation of the solution film. In this case, the removal rate of silica from solution becomes faster than the dissolution rate of quartz. As a result, m_{SiO_2} in the bulk of solution has dropped below than quartz solubility even in the presence of quartz (250 and 383 days in Table, series 1). After a complete dissolution of quartz, the reaction is still in progress at the expense of a decrease in m_{SiO_2} in the bulk of solution. As this takes place, the solution arriving to the opal is saturated with silica to a lesser and lesser degree. As a result, the opal re-crystallizes back into quartz and the solution becomes depleted of silica (the last run in Table, series 2). Thus, the quartz-water equilibrium turns into disequilibrium state under the action of surface forces.

With respect to the above hypothesis, the lack of distinct time dependence of m_{SiO_2} (fig.) is explained by the fact that different crusts formed above the meniscus are attached to the ampoule walls with different forces. The weakly attached crusts can fall down, dissolve, and raise m_{SiO_2} accidentally. As a result of this “natural selection”, only the crusts strongly attached to the ampoule walls are retained in very long experiments. Different materials of ampoules are unlikely to be concrete reason of variation in m_{SiO_2} as distinct influence of this factor on m_{SiO_2} was not observed (Fig.). Roughness of inner ampoule walls may be considerably more important factor. It can influence the reaction intensity

through various wetting extent of the walls with solution and various attachment forces of the crusts to the walls.

Disequilibrium between the secondary quartz above the meniscus and the bulk of solution can be supported during any long time as the silica movement between them can be realized only in one direction towards quartz. Such ordering of inner structure is typical for dissipative systems [15]. However in contrast to usual dissipative systems formed under open conditions far from equilibrium, our system begins to form under closed conditions at equilibrium. Because almost all minerals are well wetted with water, this phenomenon can be widespread under both experimental and natural conditions. This circumstance must be kept in mind in the studies of equilibria, kinetics, and mechanisms of reactions of various minerals with two-phase fluids.

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