QUARTZ INSTABILITY IN WATER AT 300 - 400°C

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At the present time low quartz (α-quartz) is believed to be stable mineral at least to 573°C and 20000 bars [1]. Recently we have published experimental results suggesting that at 300°C and 88 α-quartz is metastable and transformed into chalcedony-like mineral [2]. In this work new data are presented on this problem.

The experiments were fulfilled by quenched method in hermetically sealed gold ampoules during longer period of time than earlier. At each temperature two series of experiments were fulfilled. In one series an ampoule was equipped with water and quartz crystal with mass far beyond than is required for saturation of water with silica. In another series an ampoule was equipped with water and crushed quartz (20-50μ) with mass only two times greater than is required for saturation of water with silica at the temperature of experiments. In the case of proceeding of expected reaction, we projected to obtain new mineral in sufficient amounts for analyses in the first series and to measure its solubility in the second series.

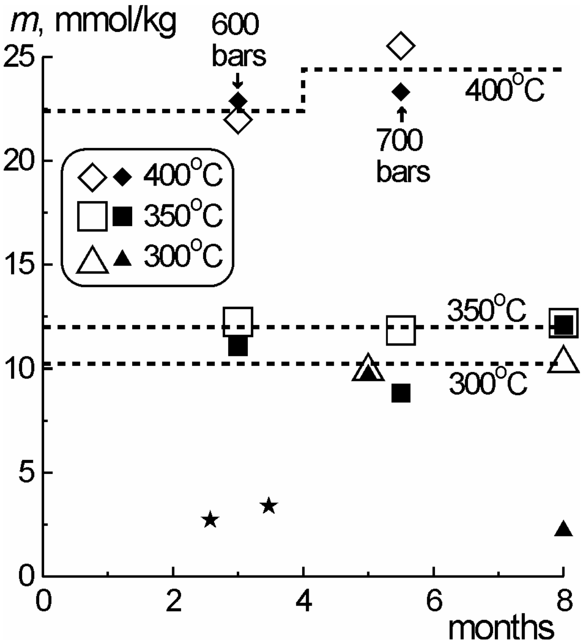


Fig.1. Concentrations of dissolved silica at various temperatures in experiments with quartz crystals (empty symbols) and with crushed quartz (filled symbols). The stars show old experimental results at 300°C with another crushed quartz in platinum ampoules [2]. Dashed lines show quartz solubility [3].

After 5 months at 300°C, aqueous silica concentration in both series was equal to quartz solubility (fig.1). What this means is the lack of expected reaction. Earlier under analogous conditions after 3 months, crushed quartz was completely transformed into chalcedony-like crusts with solubility lower than quartz (shown by stars). Distinction in experimental results can be explained by two distinctions in experimental conditions: 1) the use of different specimens of quartz and 2) the use of different materials of ampoules: platinum earlier and gold now. After 8 months at 300°C in experiment with crushed quartz, silica concentration in water dropped by a factor of 4.5 as compared with quartz solubility (filled triangle) and quartz itself was transformed completely into chalcedony-like crusts. During the same time in experiment with quartz crystal, silica concentration in water remained at a level of quartz solubility (empty triangle). The main body of crystal was retained but part of it was transformed into the same chalcedony-like crusts. In this experiment the reaction proceeds at silica concentration equal to quartz solubility. That is quartz crystal dissolved considerably faster than new mineral precipitates. It is precipitation of new mineral controls the rate of overall transformation reaction.

According to the data of scanning electron microscopy (SEM), the crusts formed at 300°C after 8 months have bud-like, needle-shaped, hole-shaped, and fold-shaped structures (fig.2). Morphological variety of the crusts suggests that in spite of long-term experiment, the transformation process has yet to be completed. According to the data of infrared spectroscopy and X-ray diffraction, the crusts are defined as crystobalite-tridymite opal.

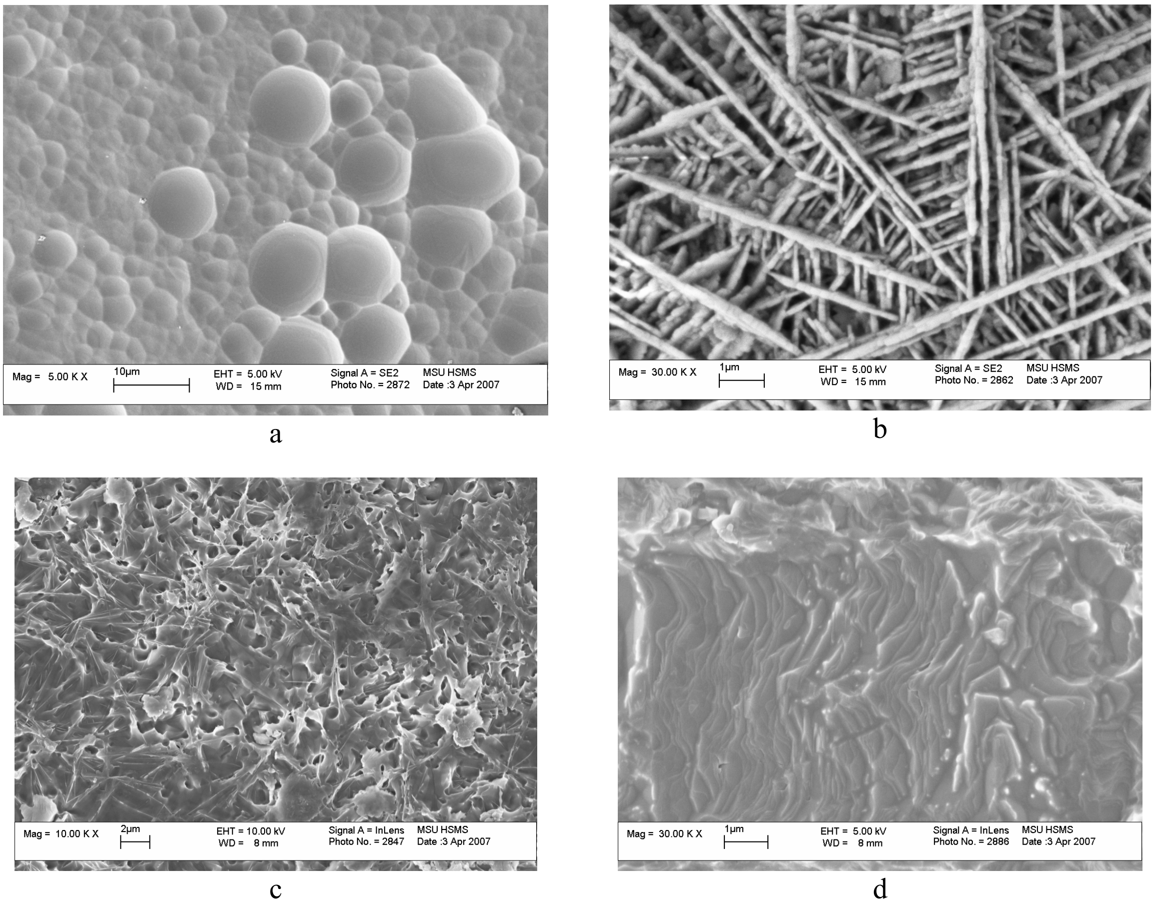
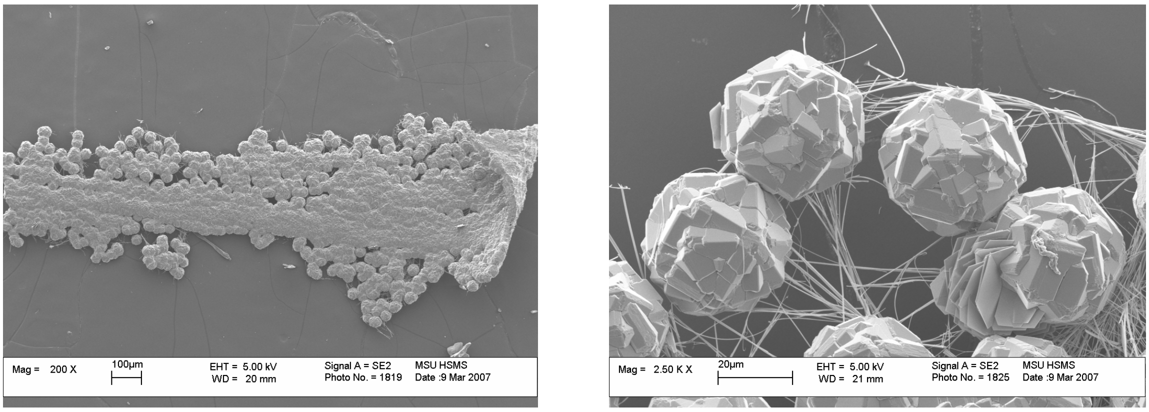


Fig.2. The surface of crusts in experiment with crushed quartz at 300°C (8 months): a - buds, b - needle-shaped crystals, c - hole-shaped structure, d - fine folds

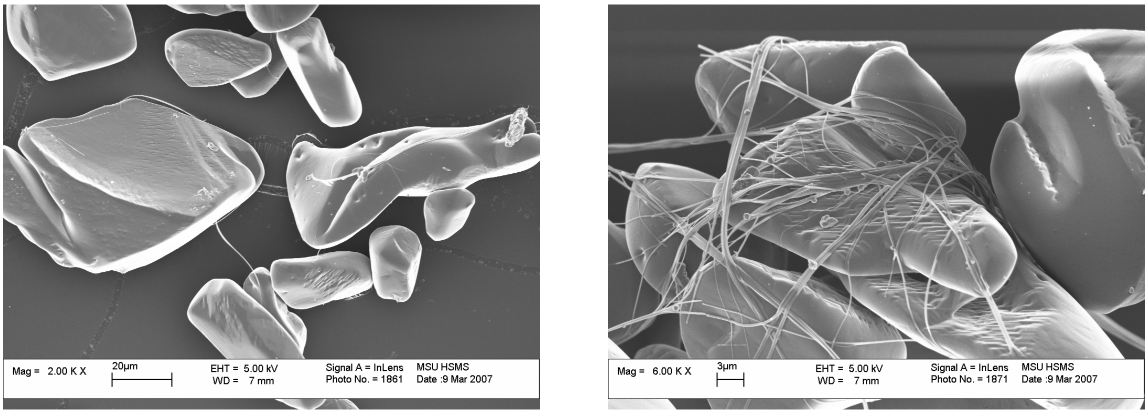
At 350°C in all experiments with quartz crystals (empty squares in fig.1), the concentration of dissolved silica was equal to quartz solubility, and crusts were not formed. In the series with crushed quartz (filled squares in fig.1), the crusts were formed only in experiment lasted 5.5 months, and just in this experiment the concentration of dissolved silica was distinctly lower (70% of quartz solubility). In more prolonged experiment (8 months) the crusts were not formed. The only distinguishing feature of experiment with 5.5 months duration can be significant roughness of inner ampoule walls. Under the deficit of suitable surface sites of quartz for nucleation of new phase, the increased roughness of ampoule walls can be a contributory factor for the formation of this phase. According to SEM data, the crusts formed at 350°C in experiment with crushed quartz are rather uniform and composed of spheres about 30 microns in size (fig.3a). One can see at the crust edge that spheres consist of isometric crystals grown together and are connected by thread-like crystals (fig.3b). According to the data of X-ray energy dispersive analysis, the crusts composed of isometric crystals contain only silicon and oxygen with atomic ratio of 1:2. The thread-like crystals contain calcium in addition to silicon and oxygen (Si/Ca = 1.5-3). These calcium silicates were formed evidently as a result of side reaction of dissolution of calcite presented as impurity in initial quartz.

At 400°C differences in concentrations of dissolved silica between experiments with crystals and crushed quartz were minor, within the accuracy of the analysis (fig.1). Slightly higher concentrations in the experiments with 5.5 months duration are explained by higher pressure. The fact is that the pressure in these experiments was initially set as 1000 bars by fraction of water in the inner volume of autoclave. This method has rather large error. After experiments we had a chance to define pressure more precisely using the pressure dependence of quartz solubility [3]. As a result we obtained 600 and 700 bars for experiments with 3 and 5.5 months duration. After all experiments with crushed quartz at 400°C, solid phases looked identical. Typically they were pieces of initial quartz with rounded ridges as a result of partial dissolution (fig.4a). Some pieces were wound with thread-like crystals of calcium silicates (fig.4b). At 400°C the crusts of chalcedony-like mineral were not found in experiments neither with crystals nor with crushed quartz.



a b

Fig.3. The surface of crusts in experiment with crushed quartz at 350°C (5.5 months): a - the general view, b - the edge of the crust at higher magnification



a b

Fig.4. Solid phases in experiment with crushed quartz at 400°C (5.5 months): a - pieces of initial quartz with rounded ridges as a result of partial dissolution, b - the same pieces are enmeshed with thread-like crystals of calcium silicates

In such a manner the stability field of chalcedony-like phase includes 300 and 350°C, but excludes 400°C. Now we plan experiments to determine lower temperature limit of the stable silica phase, to measure its solubility, and to study it using methods of X-ray diffraction analysis, infrared spectroscopy, and electron microscopy.

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