PRECIPITATION OF SILICA FROM SOLUTION UNDERSATURATED WITH RESPECT TO QUARTZ

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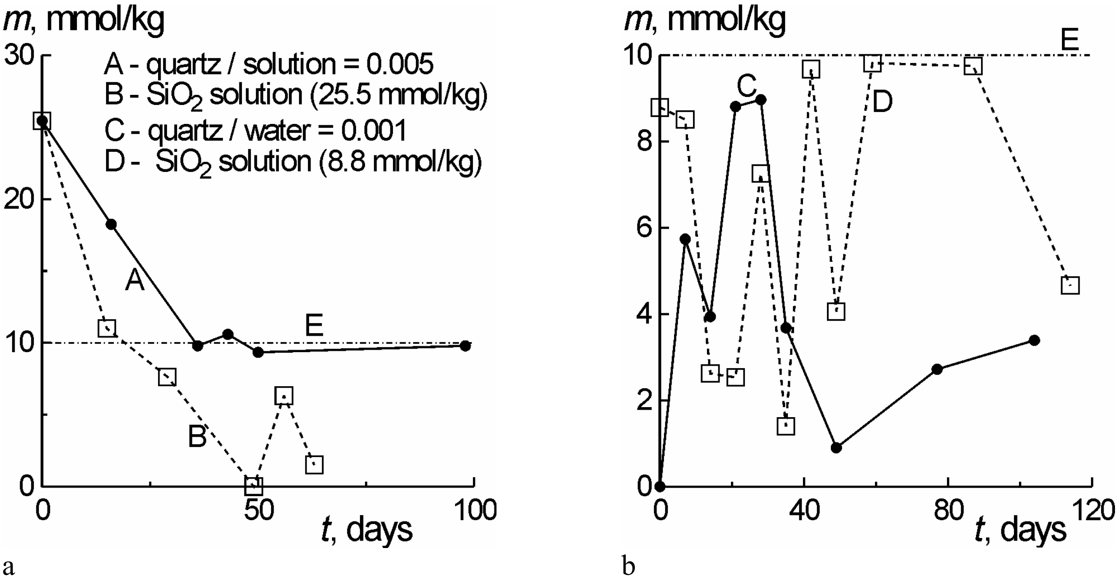
At subsurface conditions, stable modification of silica is believed to be α-quartz [1]. The results of our experiments given below are in conflict with this point of view.

Experiments were conducted in sealed platinum ampoules by quenched method at temperature of 300°C and pressure of water-saturated vapor (88 bars). After a given run duration, solid phases were separated from solutions on nuclear ultra filters with pore size of 0.03 μm. The solutions were analyzed for silica by inductively coupled plasma emission spectrometry.

Four series of experiment have been performed. In series A and B silica was precipitated from solution supersaturated with respect to quartz. The solution was obtained by dissolution of quartz glass in water. In series A with quartz besides solution, silica concentration in solution decreased with time and then it was stabilized at the level of quartz solubility (Fig. 1a). In series B free of quartz, concentration of dissolved silica has dropped below quartz solubility. This unexpected result initiated setting up the following series of experiments.

In series C, initial materials were quartz (grain size is 20-50 μm) and water. Their mass ratio (0.001) provided an excess of silica with respect to quartz solubility by 67%. In this series, concentration of dissolved silica at first increased but then stopped reaching quartz solubility and decreased (fig. 1b). In series D free of quartz, there was only solution slightly undersaturated with respect to quartz. Here time dependence of concentration had a saw-shaped character. Such peculiarity is character for colloid system in which fine solid particles can be aggregated or, in contrast, separated as a consequence of accidental reasons [3]. As a result, the particles accordingly are held back on filter or pass though it yielding additional contribution in solution analyses. Run duration in both series was insufficient to reach equilibrium.

An investigation in scanning electron microscope has shown that at the beginning of series C and D a new precipitate was represented by rolled ribbons ("shaving") (fig. 2a). At the end of series C, precipitate was represented by crusts. Outside surface of the crust facing to solution consists of buds (fig. 2b). On inside surface of the crust facing to ampoule wall, concentric zonal structures are seen (fig. 2c). These agate structures were obtained at constant external conditions, i.e. the cause of their formation is obviously related to internal self-organization of the system [4]. At the end of series D, precipitate was represented essentially by "shaving" but the were some crusts composed of crystals grown together with size of 0.1-2 μm. Large crystals grew disorderly and small crystals formed bunches of linear chains (fig. 2d).



a b

Fig.1. Silica concentration in solution vs. time in series A, B (a) and C, D (b). The line E corresponds to quartz solubility [2].

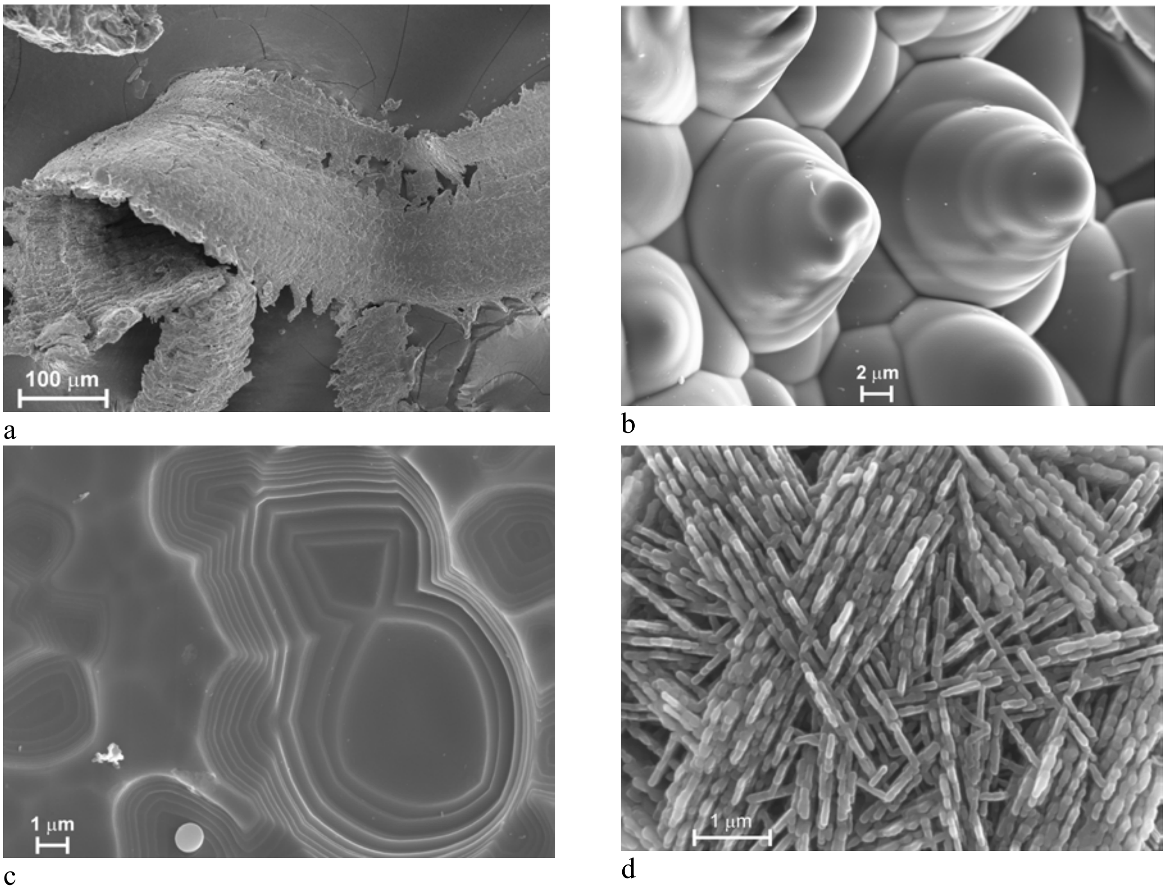


Fig.2. Images of precipitates in scanning electron microscope: a – rolled ribbon (“shaving”) at the beginning of series C and D; b and c – outside and inside surface of crust at the end of series C; d – crystalline crust at the end of series D.

There are some features of existence of gel-like stage in precipitate formation. They are: thin threads connecting crack edges in deformed “shaving”; unclear, translucent structures of crust; defects of crust surface only close to aggregates of fine particles; clearances between zones.

X-ray energy dispersive analysis has shown that crust composition from series C and D corresponds to formula SiO_2. X-ray powder diffraction analysis did not give diffraction lines on roentgenograms indicating roentgen amorphous precipitates. At the moment we try to investigate precipitate structure using electron diffraction. Experiments for determining stability field of new phase, its thermodynamic and kinetic characteristics, reaction mechanisms are planning.

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