## DISTINCTION BETWEEN MECHANISMS AND RATES OF QUARTZ–WATER REACTION IN A FORWARD AND REVERSE DIRECTION V.A.Aleksevev, L.S.Medvedeva, Y.G.Tatsii

Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, Moscow

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The influence of solution saturation state on the rate of quartz–water reaction  $SiO_2 + 2H_2O = =H_4SiO_4^{0}$  is expressed by the following equation [1-3]:

$$dm/dt = k_d (1 - m/m_{eq}) S/M, \qquad (1)$$

where m and  $m_{eq}$  are the actual and equilibrium concentrations of silica in solution (mol/kg); t is the time (sec);  $k_d$  is the dissolution rate constant (mol m<sup>-2</sup>sec<sup>-1</sup>); S is the surface area of a mineral (m<sup>2</sup>); M is the mass of water (kg). The overall reaction rate expressed by equation (1) is considered as a rate difference of forward and reverse reactions:

$$dm/dt = k_{d}S/M - mk_{p}S/M, \qquad (2)$$

where  $k_p$  is the precipitation rate constant (kg m<sup>-2</sup>sec<sup>-1</sup>). The identity of the equations (1) and (2) is provided using a principle of microscopic reversibility (or detailed balancing) [2]:

$$m_{eq} = k_{d}/k_{p}.$$
 (3)

The acceptance of this principle means an assumption that processes of mineral dissolution and precipitation proceed through a series of common elemental steps one of which controls the rate of the both processes. Due to the principle of microscopic reversibility, the equation (1) is used for the description of not only kinetics of quartz dissolution ( $m < m_{eq}$ ) well investigated experimentally, but also and kinetics of its precipitation ( $m > m_{eq}$ ) with few experimental data.

To fill this gap and to test the validity of the above-mentioned principle, we have carried out experiments with quartz and water (ratio of masses is 0.5) in platinum ampoules. These experiments have shown that the needed time to reach equilibrium from above is greater than that from below by approximately two orders (fig. 1). Unexpected circumstance was that approaching from below, measured silica concentrations in solution flatten out above an equilibrium concentration and the more is pore size of the filter, the higher are these concentrations (series B and C). This is indicative of ultra fine quartz particles yielding an additional contribution to the results of solution analyses (inductively coupled plasma spectrometry). As judged from the divergence of curves B and C with time, these particles are not primary, but formed during dissolution. They are likely to separate from the surface of large pieces as a result of preferential dissolution of micro cracks formed during quartz crushing. To diminish the influence of these particles, we have used more rough quartz fraction. This led to lowering silica concentration in solution (series D).

However, there was a suspicion that ultra fine particles distorted the shape of kinetic curves for this fraction also. Because of this, we treated the rough quartz fraction in addition with fresh batches of water (5 times each during 3 days) at 250°C. After such treatment, the initial dissolution rate of this fraction has indeed decreased in 30 times (series D' in fig 2 in comparison with series D in fig 1). For series D', seven values of  $k_d$  are calculated using the integrated form of equation (1):

 $k_d = -m_{eq}/t/(S/M)ln((1-m/m_{eq})/(1-m_0/m_{eq})), (4)$ where  $m_0$  is the initial silica concentration in solution (mol/kg). The mean value of  $k_d$  is  $(9.7\pm2.2)\times10^{-11}$ mol m<sup>-2</sup> sec<sup>-1</sup>. It practically coincides with the published dada [3]. The quantity m can be calculated from the equation (4) after its transformation:

 $m = m_0 \exp U + m_{eq}(1-\exp U),$  (5) where  $U = -t(k_d/m_{eq})(S/M)$ . The curve D' (fig. 2) relevant to the equation (5) with  $m_0 = 0$ ,  $S/M = 20 \text{ m}^2$  $kg^{-1}$ ,  $m_{eq} = 0.00214$  mol/kg and the above-mentioned value of  $k_d$ , well describes the experimental data approaching to equilibrium from below.

Use of the same  $k_d$  value for the description of quartz precipitation kinetics ( $m_0 = 0.0065 \text{ mol/kg}$ ) yields a curve E" that contradicts to the experimental data sharply (series E' in fig. 2). Thus, it is impossible to describe kinetics of both processes with the help of the equation (1). It means that the precipitation of quartz proceeds through other mechanism than its dissolution. It is evident that the ultra fine particles of quartz and unevenness on its larger grains are active sites for precipitation. Previous hydrothermal treatment of crushed quartz grains causes the dissolution (disappearance) of these active sites. As a result the precipitation of silica is sharply retarded. The fact that silica concentrations during approach to equilibrium from above (series E' in fig. 2) stay too long at a level of solubility of  $\alpha$ -cristoballite, suggests that this metastable modification of silica can precipitate instead of quartz.

1. *Rimstidt J.D., Barnes H.L.* Geochim. et cosmochim. acta. 1980. v. 44. N 11. pp. 1683–1699.

2. Lasaga A.C. Rev. Mineral. 1981. v. 8. pp. 135-169.

3. Bird G., Boon J., and Stone T. Chem. Geol. 1986. v. 54. N 1/2. pp. 69–80.



Fig. 1. Dependences of aqueous silica concentrations on time in quartz–water system at 150°C. The initial quartz grains were ultrasonically cleaned from ultra fine particles by water. The empty and filled symbols mean an approach to equilibrium from above and from below. The vertical lines with bars designate the scatter limits of the published values of  $\alpha$ -quartz (Qtz) and  $\alpha$ -cristoballite (Crs) solubilities

Fig. 2. The same as fig. 1 for series D and E, but initial quartz grains were treated in addition with fresh batches of water (5 times each during 3 days) at 250°C. The curves D' and E'' correspond to the equation (5) with  $m_0 = 0$  and 0.0065 mol/kg.