

THE STRUCTURAL EQUILIBRIA IN SILICATE MELTS: APPLICATION TO PETROLOGICAL ESSENTIAL HETEROGENEOUS REACTIONS

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The simulation of igneous processes in the natural magmatic systems often requires a recognizing of a mechanism of reactions between solid phases and melt components. Especially it is important for processes occurring in open systems with varying conditions. But identification of melt species involving in heterogeneous reactions is generally uncertain. Theory of the atomic structure of silicate melts are based on laboratory studies using nuclear magnetic resonance (NMR), vibrational spectroscopy and Raman scattering spectroscopy (e. g. Mysen, 1990). It is known that the melts (glass materials) are characterized by absent of long-range ordering. But the net structure of silicate melt consists of structural units resembling of unit cells of main silicate minerals – Q^4 , Q^3 , Q^2 , Q^1 , Q^0 (index means the number of bridging oxygen in the structural unit) The above structural units have a short live time ($\sim 1 \mu s$), and they always exchange for bridging $[BO]^0$ and non-bridging oxygen $[NBO]$ with each other. It is supposed that such permanent reconstruction of melt structure is the main mechanism of a viscous melt flow (Liu et al., 1988).

The structural disproportionation equilibria $2Q^n = Q^{n-1} + Q^{n+1}$ with $n = 1, 2, 3$, are described for modeling of liquid silicates in homogeneous silicate systems – glasses. But similar structural equilibria have not been used for characterization of heterogeneous chemical reactions and phase equilibria in multi-component silicate systems until now. Insufficient resolution of spectroscopic and scattering methods does not allow the direct determination of structural complexes in multi-component systems. The NMR spectroscopy technique is more sensitive for analysis of composed system, but such type of NMR-data are not sufficient still. Usually the melt species composition is guessed on the basis of all compounds, occurring in studied systems.

The simulating of liquidus phase equilibria in heterogeneous silicate systems based on principle about equality in chemical potentials for liquid and solid phases on the liquidus. The calculations are reduced to determination of melt species distribution on the basis of the mixing Gibbs free energy minimization for the whole melt species combination (e. g. Ghiorso, 1985). However, if a chemical reaction runs in the system, the Gibbs free energy change of the reaction has to take into account in that causes.

The main idea promoted here consists in that the “chemical-structural” equilibria (reactions) could occur in multi-component silicate melts. Thermodynamic effect of such reactions may be more considerable then the mixing effect only. The first attempt to construct some structural equilibria in heterogeneous multi-component silicate systems having a petrological interest is made (Khleborodova, 2010), that included 1) the estimation of relative chemical affinity of network modifying cations to some structural units, deriving from the structural unite distribution in the simple silicate systems studied earlier and available from literature (e. g. Mysen, 1990; Maekawa et al. 1997; Neuville et al., 2008) 2) simulation of structural equilibria of An-Fo-melt and Ab-An-Di-melt reactions, using the new structural equilibria $Q^0 + Q^4 = 2Q^2$ and known structural equilibrium $2Q^3 = Q^2 + Q^4$ 3) the calculation of the enthalpy change ΔrH , Gibbs function change ΔrG and constants K of these equilibriums using thermodynamic data (Holland&Powell, 1998), 3) the analyses of these equilibria behavior in heterogeneous aphybasaltic systems undergoing varying conditions.

The simulated heterogeneous reactions were examined in aspect of theirs application to some petrological processes, running at nonequilibrium conditions, specifically the melt-wall rock and melt-fluid interaction under pressure and temperature gradients. The some geochemical trends of magmatic differentiation of high magnesia rocks of North Kamchatka group volcanoes are shown in this respect.

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