THE EFFECT OF ALUMINIUM ON MECHANISM OF WATER WITH SILICATE MELT (PMR SPECTROSCOPY)

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The preliminary experiments on study of the state dissolved water in aluminosilicate glass were done by proton magnetic resonance method (PMR).

In PMR-spectra of all investigated aluminosilicate glasses of preparing samples, one should emphasize two typical features which are absent in purely quartz glasses:

1) presence of a rather narrow signal (~1khz) having a thin structure;

2) appearance in the spectrum of the additional superwide component which manifests itself especially markedly at low (T<150K) temperatures.

Thus, it is experimentally determined, that the addition of even a small quantity of Al into quartz glass results in the appearance of two additional signals in their PMR-spectra.

One should point out, that in one of the studied samples of water-bearing quartz glass there was a narrow signal and it was as predominating in the spectrum; however, it had no a thin structure. That sample was obtained at an early stage of fluid intrusion into the melt.

Unfortunately, strict quantitative calculations of the integral intensity of the narrow signal relative regularities manifest themselves in the spectra rather markedly.

A narrow signal is rather sensitive to the technique of preparing the sample: its intensity is high when the sample was made at T=1200^{o}C and P=2kbar, and decreases by several times at T=1300^{o}C and P=4kbar. A growth of intensity of the narrow component at the increase of water content in the aluminosilicate glass is also observed. Its temperature behavior is distiinguished by a sharp hysteresis : a signal exists up to T~240K (the intensity drops with temperature decrease), but at heating it occurs by leaps at T~275K. In contrast to quartz glass where a narrow signal represents a singlet, in aluminosilicate this line of PMR-spectrum has a complex structure and at division of contours by GRAMS program it is best described by the superposition of the three Gauss-Lorentz curves.

The available experimental date allow one to assume that a narrow signal in PMR-spectra of the studied aluminosilicate glasses is formed by water macroclusters, consisting of several hundreds of water molecules. A smooth decrease of its intensity with temperature decrease seems to be explained by the distribution of macroclusters in size sample volume: the less is the macrocluster size, the lower is the temperature of water freezing there.

One should also notice a presence of chemical shifts between both the narrow component and an ordinary signal, as well as between the components of the narrow line itself. The reason for that, perhaps, is in the fact that Al intrusion changes the structure of the amorphous matrix on the surface of separation of phases water – glass in such a way that H_2O molecules of a macroclaster would interact with all the three types of atoms entering glass composition: Si, Al, O_2. It is rather probable that this reason macroclaster signal is shifted on the whole into a weak field of relatively hydroxyl lines.

In purely quartz glass the temperature behavior of the narrow signal is somewhat different than in the aluminosilicate: it exists without changing up to T~240K at cooling of the sample and rises jump wise at heating at T~275K, i.e. in this case these seems to be no macroclaster distribution in sizes. This difference gives grounds to suggest different mechanisms of water dissolution in quartz and aluminosilicate glasses.

A superwide signal manifests itself most vividly at low temperatures (T<150K). Its intensity grows with temperature decrease. Unfortunately, its separation in the pure form is far impossible. However, there are grounds to assume that it is Pake`s doublet – signal formed by the isolated water molecules.

So, the preliminary experiments it possible to assume that even a small addition of Al into quartz glass results in the abrupt cnange of melt interaction with the fluid and appearance of new extra states of water in the amorphous matrix.

An essential difference of PMR-spectra of water-bearing aluminosilicates and Na-silicates is observed: 1) in all obtained aluminosilicate spectra macrocluster line is present. It does not exist in Na-silicate spectra; 2) in the spectra of Na-silicates Pake`s doublet manifests markedly (especially at T<200K), whereas in aluminosilicates even at low temperatures this signal is so indistinct that it cannot be clearly referred to the isolated water molecules.

One can assume that the effect of Na and Al on interaction of the melt with the fluid differs essentially. That is why, perhaps, there are differences of Na and Al as centers of coordination.