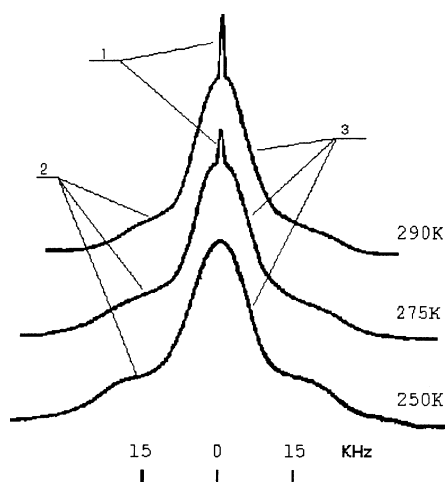


Zavel'sky V.O.¹, Salova T.P.² Peculiarities of water interaction with silicate melt in dependence on its composition (NMR study)

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Taking into account the evident fact that different species of water dissolved in glass show different number of thermally activated mechanical degrees of freedom (rotational, vibrational, etc.), it should be expected that a behavior of NMR signals from protons of these species can provide an interesting information about the state of water in silicate glasses. We studied an interaction of the aqueous fluid with alumino-silicate and silicate glasses and aqueous species in the quenched glasses. We used the method of the stationary dynamic NMR. NMR spectra were obtained using the impulse NMR-spectrometer CXP-200 (Bruker). The NMR frequency was 200 MHz. All spectra NMR for ²³Na were obtained at room temperature (~287 K). The proton spectra were registered in the temperature interval 135 – 475 K. Variation, stabilization, and control of temperature were done using the regulated thermoblock B-VT



1000 (Bruker). An accuracy of temperature measurements was $\pm 2^\circ\text{C}$.

As a result of the study of water-bearing alumino-silicate and silicate glasses, we found

1 – 4 types of inclusions of non-dissociated water were revealed: a) water in bubbles, b) water macroclusters, c) water macroclusters with strong hydrogen bond, d) isolated water molecules (Fig. 1);

2 – in Na-silicate melts, Na ion is accommodated in structure by two ways: a) with the formation of the covalent bond Si-O-Na, b) enters into oxygen environment formed by bridge oxygens; Na ions of the second type serve as coordination centers for water molecules (Figs. 2, 3, 4, 5);

3 – in quartz glass, water is completely dissociated and exists as chemically identical hydroxides distributed inhomogeneously in the glass volume (Fig. 6);

4 – incorporation of Na and (or) Al ions into the quartz glass results in appearance in the amorphous matrix of additional water species. Na and Al ions become coordination centers for non-dissociated water molecules. As the coordination centers, these ions are different. Al, apparently, forms appreciably larger coordination aggregates in comparison to Na (Fig. 7).

Fig. 1. Thermal dependence of ¹H NMR spectrum of water-bearing albite glass (8.8 wt. % of H₂O): (1) signal of water in bubbles; (2) – Pake's doublet (molecular water); (3) central line (macrocluster water).

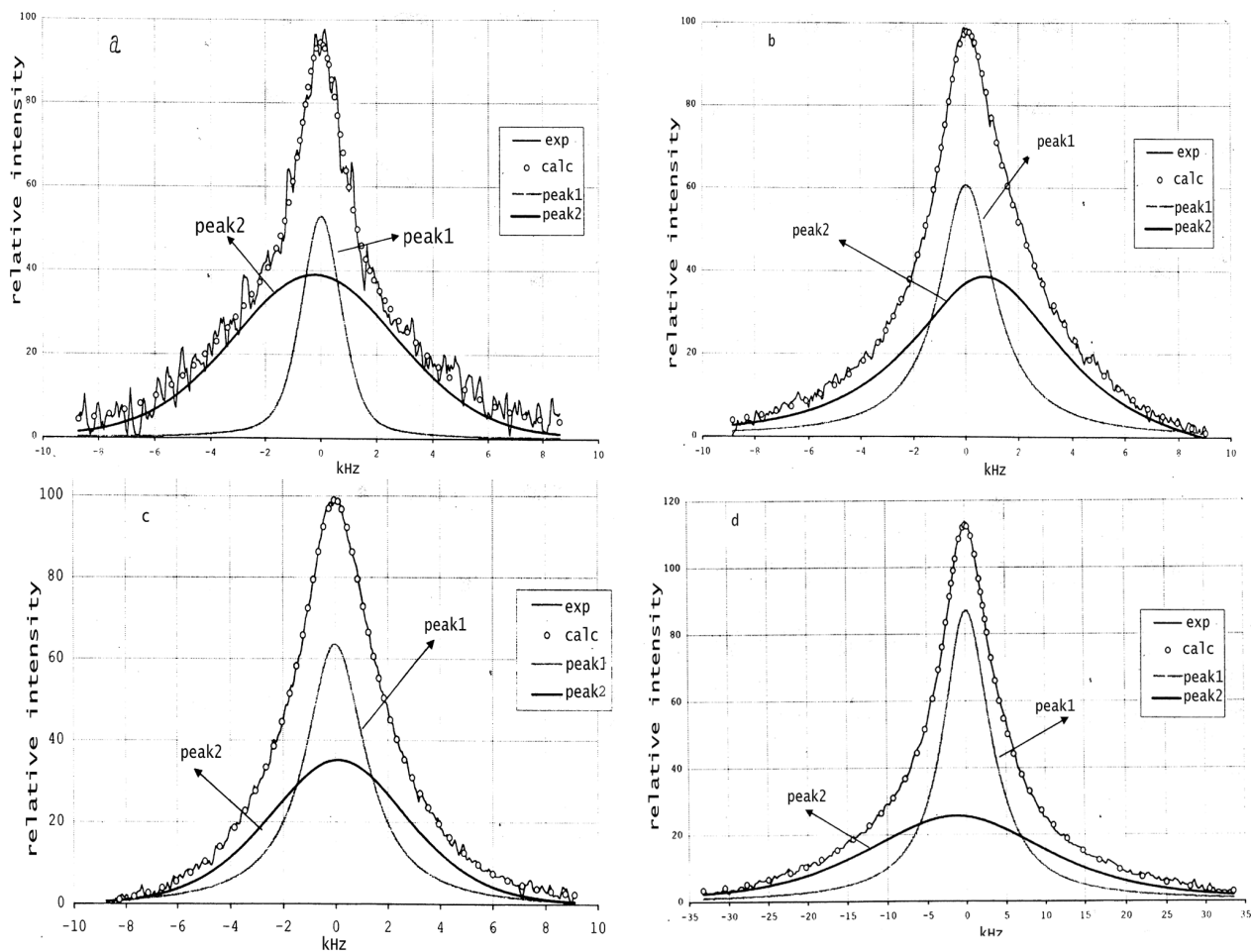


Fig.2. The NMR ^{23}Na spectra of glasses $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ with different water content and their splitting into two components: peak 1 – signal of Na, situated in the oxygen environments; peak 2 – signal of the covalent-bonded Na ion from the Si-O-Na fragment. a) $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ – unhydrous; b) $\text{Na}_2\text{O} \cdot 3\text{SiO}_2 + 2.9$ wt. % of water; c) $\text{Na}_2\text{O} \cdot 3\text{SiO}_2 + 5.6$ wt. % of water, d) $\text{Na}_2\text{O} \cdot 3\text{SiO}_2 + 9.4$ wt. % of water.

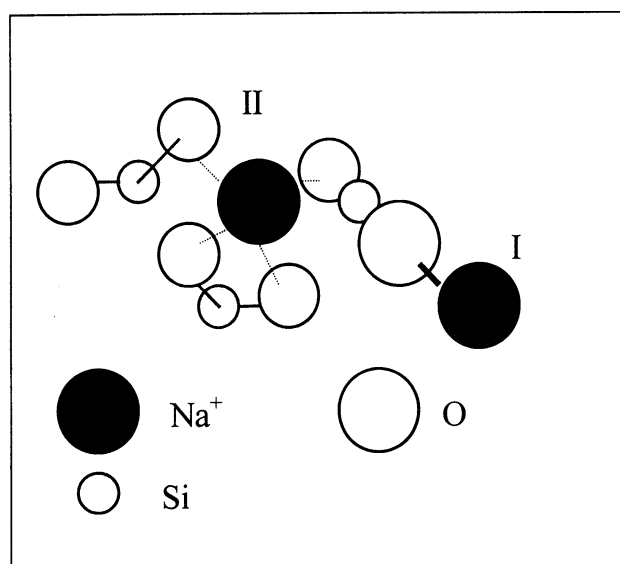


Fig. 3. Scheme illustrating an enter of Na into the glass structure: I – with break of the bridge Si-O-Si bonds and formation of Si-O-Na; II – accommodated in the oxygen environment formed by the bridge oxygens.

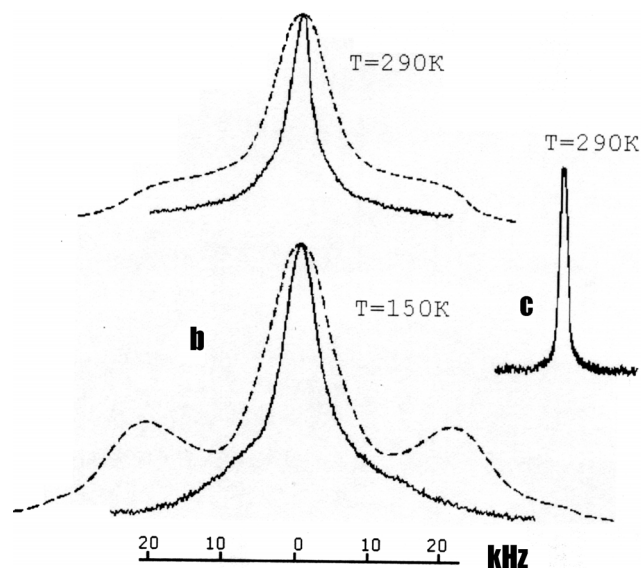


Fig. 4. The ^1H NMR spectra of water-bearing quartz and albite (dashed line) glasses at different temperatures (a, b); c – the signal obtained as a result of the impulse narrowing of line in quartz at $T = 290$ K.

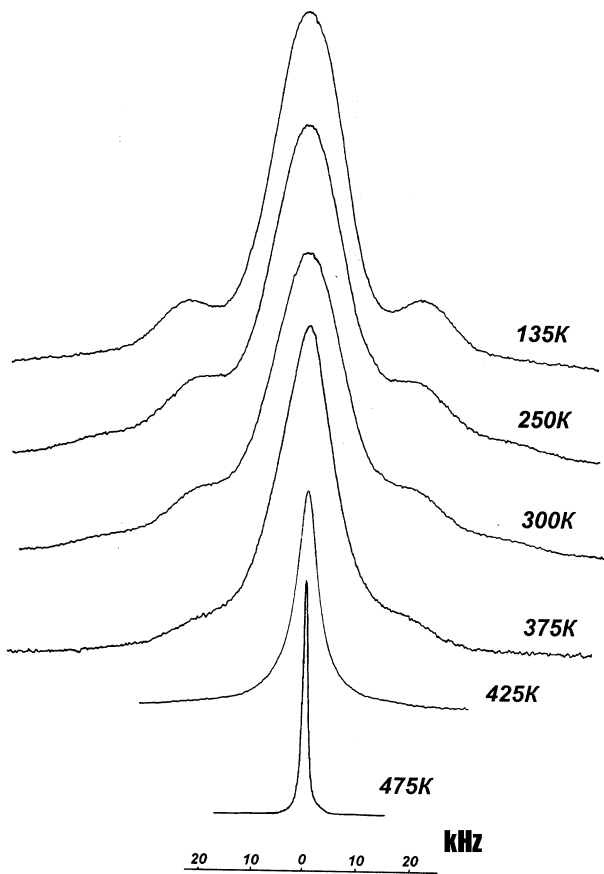


Fig. 5. $\text{Na}_2\text{O} \cdot 3\text{SiO}_2 + 9.4$ wt. % of water; thermal evolution of the NMR-spectra.

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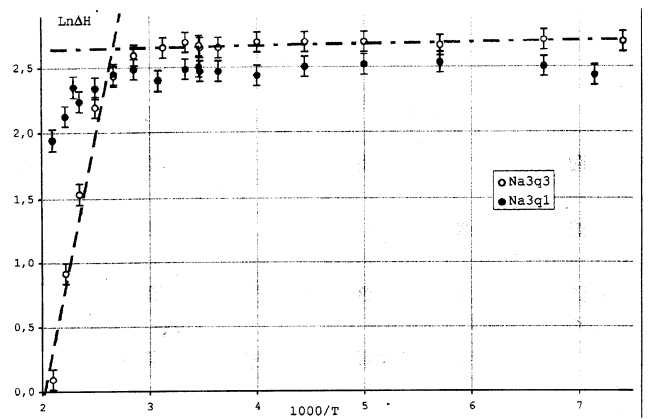


Fig. 6. Dependence of width of the central line of the ^1H NMR spectrum on inverse temperature ($103/\text{TK}$) in samples $\text{Na}_3\text{q1}$ ($\text{Na}_2\text{O} \cdot 3\text{SiO}_2 + 2.9$ wt. % of water) and $\text{Na}_3\text{q3}$ ($\text{Na}_2\text{O} \cdot 3\text{SiO}_2 + 9.4$ wt. % of water).

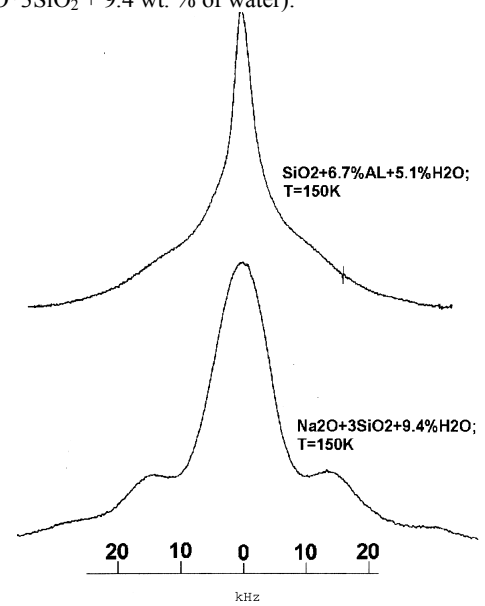


Fig. 7. The NMR spectra of water-bearing alumino-silicate and Na-silicate glasses.