

Structural state of iron ions in the glasses of granitoid composition synthesized at various T - fO_2 conditions

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Mössbauer study of the experimental glasses of granitic and pantelleritic compositions obtained by quenching of melts exposed at various T - fO_2 conditions (1200–1420°C, 10^{-12} – $10^{-0.7}$ bar) showed that Fe^{2+} ions are distributed mainly on the octahedral (and/or five-coordinated) positions, regardless of the Fe^{3+}/Fe^{2+} in the melt (glass), and play the role of modifier cation. Coordination of Fe^{3+} ions depends on the degree of oxidation of the iron atoms. With increasing fraction of ferric iron, its coordination changes from octahedral to tetrahedral. Thus, being a network-modifying cation under reducing conditions, Fe^{3+} becomes predominantly a network-former under oxidizing conditions. The structural role of Fe^{2+} as network-modifying cations does not change fundamentally with variations in the degree of iron oxidation. The change of Fe^{3+} coordination in aluminosilicate melts of various compositions occurs at similar values of $Fe^{3+}/\Sigma Fe \geq 0.5$.

Key words: iron ions, structural state, silicic aluminosilicate melts, glasses, Mössbauer spectroscopy

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The structural state of iron ions was studied by Mössbauer spectroscopy in glasses quenched from natural silicic aluminosilicate melts of granite (I2) and pantellerite (P9) compositions exposed to various T - fO_2 (1100–1420°C, 10^{-12} – $10^{0.68}$ bars) conditions at a total pressure of 1 atm. [Volovetskii *et al.*, 2012]. Processing and analysis of the Mössbauer spectra included the reproduction of two independent distributions $p(\epsilon)$ of quadrupole splitting, ϵ , corresponding to Fe^{3+} and Fe^{2+} , because this parameter is the hyperfine interaction is most sensitive to the geometry of the surrounding. The linear correlation of parameters was taken into account for the distribution function of the hyperfine parameters Fe^{2+} : the quadrupole splitting (ϵ) and the Mossbauer isomer shift (δ) [Rusakov, 1999, 2000]. The crystal-chemical identification of partial Mössbauer spectra was performed by comparing the obtained isomer shifts, δ , for ^{57}Fe nuclei in the samples with the results of the Mossbauer and X-ray investigation of a large set of crystal phases of various mineral systems [Menil, 1985; McCammon, 1995]. The rate of structural equilibration in melt is much higher than that of melt–gas (air furnace) equilibration. This allowed us to use some glasses obtained under nonequilibrium conditions for the assesment of the influence of the degree of iron oxidation on its structural state in melts.

Fig. 1 shown the Mössbauer hyperfine parameters, quadrupole splitting (ϵ) and isomer shift (δ), of the synthetic quenched glasses, which can be used for the estimation of the structural state of iron ions. Also shown are the ranges of isomer shifts typical of oxygen environments of iron in different valence state in crystalline materials (octahedral, five-coordinated, and tetrahedral). It should be noted that the range of five-coordinated Fe overlaps with the ranges of octahedral and, to same extent, tetrahedral positions; therefore the range of δ corresponding to the five-fold coordination cannot be distinguished.

The ϵ and δ values of Fe^{2+} in the two series of quenched glasses, I2 and P9, vary in a narrow ranges (Fig.1) and do not change significantly depending on fO_2 and T . The isomer shift values correspond mainly to six- and five-coordinated Fe^{2+} . Much more significant variation were observed for the parameters of Fe^{3+} . The quadrupole splitting for Fe^{3+} in the series I2 glasses are, in general, approximately 0.2 mm/s higher than those in the series P9 glasses, which could be related to a more heterogeneous local environment of Fe^{3+} in the granitic glasses (Fig.2).

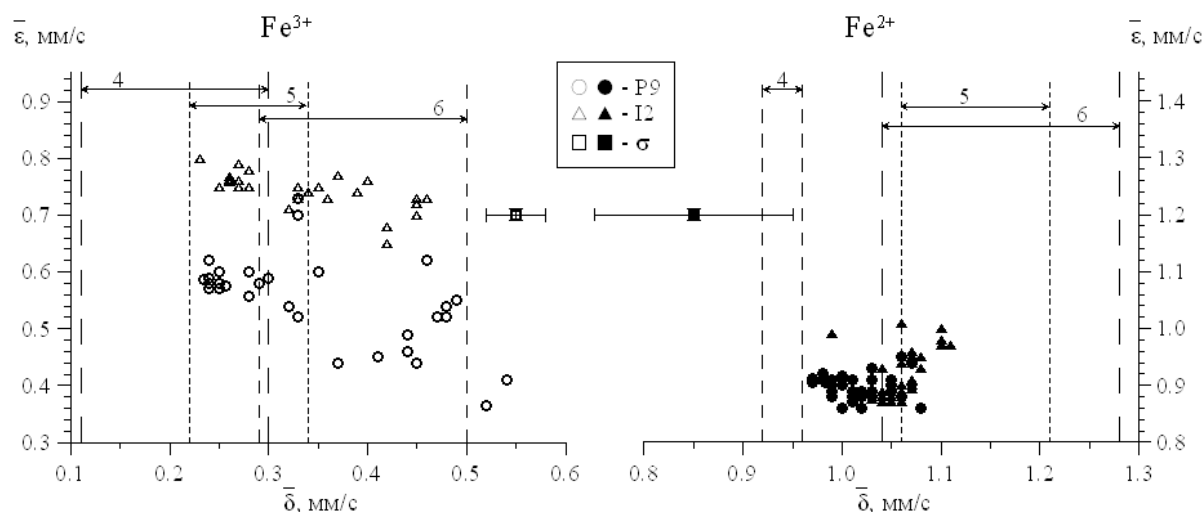


Fig.1. Hyperfine parameters of the partial spectra of Fe^{3+} and Fe^{2+} in the δ - ϵ coordinates. The maximum standard deviations of the parameters of Fe^{3+} and Fe^{3+} are shown in the diagram.

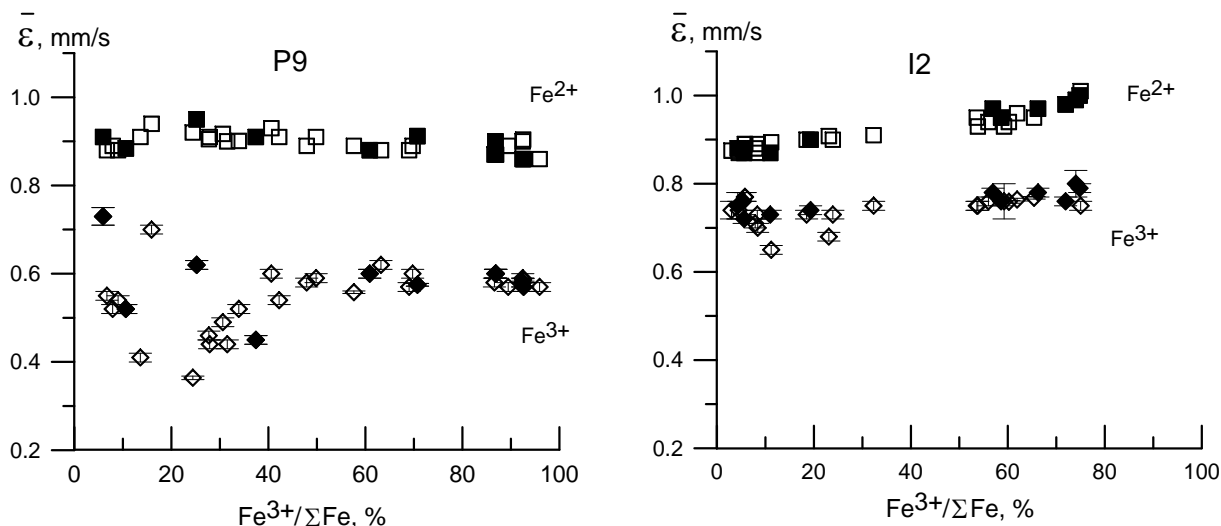


Fig.2. The dependence of the Mössbauer quadrupole splitting for Fe^{2+} and Fe^{3+} on the oxidation state of iron in granitic (I2) and pantelleritic (P9) glasses. Filled symbols – samples are closest to equilibrium with the atmosphere furnace at a temperature of the experiment.

The wide range of variations in the isomer shift for Fe^{3+} in both glass series is evidently related to a change its structural positions in melts under various redox conditions. Figure 3 shows the dependence of the Mössbauer isomer shift, δ , on the degree of iron oxidation, i.e., the content of Fe^{3+} relative to total iron in the glass. Also shown are the ranges of isomer shift typical of octahedron and tetrahedron oxygen environments of iron in different valence states in crystalline phases. In the glasses of both series, the isomer shift for Fe^{3+} increases gradually with increasing degree of iron oxidation and passes gradually, when Fe^{3+} fraction decreases below 50–45 %, from the range characteristic of octahedral oxygen environments to the range of value corresponding to tetrahedral coordination. Hence, with increasing fraction of ferric iron, its coordination changes from octahedral to tetrahedral. Degree of iron oxidation does not affect significantly the isomer shift for Fe^{2+} in the glasses of both series; its values lie within a narrow range near the lower boundary of intervals characteristic of octahedral and five-coordinated positions (Fig.3).

It can be noted that the value of isomer shifts for series P9 are slightly lower (by approximately 0.05 mm/s) than those for I2, which may indicate a difference in the local environment of Fe^{2+} and/or some variations in the length of Fe^{2+} -O bonds.

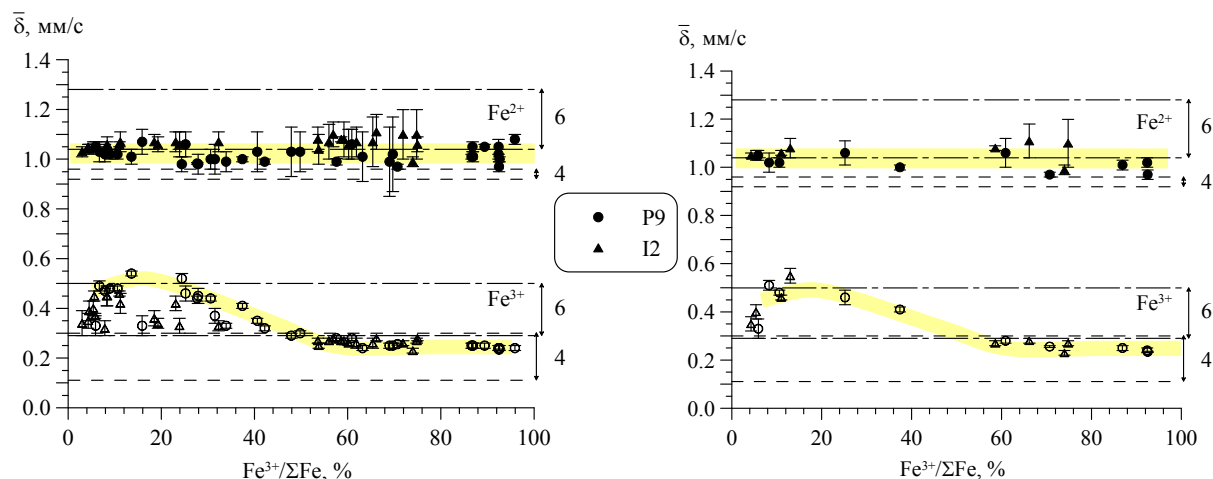


Fig.3. Dependence of the Mossbauer isomer shift for Fe^{2+} and Fe^{3+} on the degree of iron oxidation: for all samples (*left*) and for samples with the equilibrium redox state of iron (*right*)

The Mossbauer investigation of quenched granitic and pantelleritic glasses with different degrees of iron oxidation supported the previously observed phenomenon of a change in the dominant coordination of Fe^{3+} in natural and synthetic aluminosilicate melts from octahedral to tetrahedral with increasing degree of iron oxidation [Mysen, 1988]. Thus, being a network-modifying cation under reducing conditions, Fe^{3+} becomes predominantly a network-former under oxidizing conditions. The structural role of Fe^{2+} as network-modifying cations does not change fundamentally with variations in the degree of iron oxidation. The change of Fe^{3+} coordination in aluminosilicate melts of various compositions occurs at similar values of $\text{Fe}^{3+}/\Sigma\text{Fe} \geq 0.5$. For the I2 and P9 melts at temperatures of 1320–1420°C, this corresponds to $f\text{O}_2$ values higher than 10^{-5} – 10^{-3} (2–3 log units above FMQ).

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