

TEMPERATURE-INDUCED CHANGES OF THE STRUCTURAL STATE OF IRON IONS IN SILICATE MELTS (MÖSSBAUER STUDY) A.V.Polosin, A.M.Bychkov, A.A.Borisov, V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, Moscow

The temperatures of impact melts can exceed greatly the liquidus temperatures. The temperature increase induces the structural transformations and accordingly the change of density, viscosity, compressibility of liquid. The structural changes consist of a breaking up the large anions into smaller units and the rebuilding of the first coordination spheres of cations (change of coordination number, cation-oxygen bond length and cation-oxygen-cation bond angle). The first coordination sphere of iron ions relaxes a little during melt-to-glass transition (1), therefore we propose that the documented variations of mössbauer parameters characterized "quenched" phenomena in the melts. At this paper the results of mössbauer study of  $\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$  and  $1.2\text{K}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 9.2\text{SiO}_2$  glasses prepared under different temperatures are reported.

The first kind of glasses were synthesized under I220, I280, I300, I350 and I400°C. The partial pressure of oxygen was controlled by  $\text{H}_2$ ,  $\text{CO}_2$  gas mixture at one order above IW buffer level. Using mössbauer data we concluded that  $\text{Fe}^{2+}$  ions occupied four,-five and six-fold sites in the all glasses. The distribution of iron ions in each kind of sites is constant for all samples (Table I). However for every coordination isomer shift increases with the temperature of glass synthesis. The increase of IS means the decrease of the s-electron density at the nuclei of the Fe atoms. It is due most probably to the lengthening of iron-oxygen bond. It is unlikely that observed effect is a result of the quenching of heat vibrations. We proposed that the temperature-induced destruction of anions (the increase of NBO/T) documented by B.O.Mysen et al (2) for glasses of similar

composition leads to arrangement of structural units accompanied by the small lengthening of bonds.

The second kind of glasses were prepared under 1050, 1150, 1250, 1350°C and atmospheric pressure. The mossbauer spectra were fitted with two doublets. Temperature dependence of IS for two doublets differ with one increasing and another decreasing. This observation may indicate the presence of two tetrahedral sites of slightly different chemical environment. It can be proposed that iron-oxygen bond length behaves in accordance to IS.

Thus the temperature increase of silicate melt up to several hundred degrees induces the change of bond lengths for all kind of Fe sites and does not cause the change of cation coordination.

Temperature dependence of IS for ions in quenched melts

Table I

Valency	CN	S, %	IS	Regression	Correlation
CaO·FeO·SiO <sub>2</sub> glass					
2+	4	19	0.935(4)	IS=0.8I+0.00010t°C	0.78
2+	5	60	1.00(4)	IS=0.93+0.00006t°C	0.79
2+	6	9	1.16(1)	IS=1.02+0.00011t°C	0.74
1.2K <sub>2</sub> O·Fe <sub>2</sub> O <sub>3</sub> ·9.2 SiO <sub>2</sub> glasses					
3+	4	45	0.249(5)	IS=0.22+0.00002t°C	0.74
3+	4	55	0.228(4)	IS=0.25-0.00002t°C	0.74

References:

- I.G.A.Waychunas et al, Nature, 1988, v.332, March 17, p.251-253  
2.B.O.Mysen et al, Amer.Mineral., 1985, v.70, p.487-498