

PRESSURE EFFECT ON THE $\text{Fe}^{3+}/\text{Fe}^{2+}$ RATIO IN BASALTIC MELT (EXPERIMENTAL DATA)

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This study was supported by the Russian Fundamental Research Foundation (Project No 99-05-65479)

Herald DGGGMS RAS № 5 (15)'2000 v.2

URL: http://www.scgis.ru/russian/cp1251/h_dgggms/5-2000/magm18.eng

Using Mössbauer spectroscopy technique, $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios and structural positions of ferrous and ferric iron atoms were determined in basaltic glasses synthesised by quenching of natural basalt melts at high hydrostatic pressure conditions ($P=0.16\text{--}5$ kbar, $T=1250\text{--}1350^\circ\text{C}$). The experiments were conducted in high-pressure vessel with internal heater, in which the argon served as transmitting pressure medium. The samples of basaltic glasses with the various initial ferrous/ferric ratios ($\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+}) = 0.8\text{--}0.12$) were placed in hermetic platinum capsules and maintained at given PT parameters during from 11 to 130 minutes. Treatments and analysis of Mössbauer spectra of quench glasses were conducted by recovery of two independent distribution functions of hyperfine interactions parameters of the ^{57}Fe nuclei - isomeric shift and quadrupole splitting.

The pressure increase up to 5 kbar does not result in noticeable change redox state of iron in melt (glasses) after "short" experiments (11–20 minutes duration) at a constant to temperature. The ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ in glasses after these runs corresponds to value $\text{Fe}^{3+}/\text{Fe}^{2+}$ in initial basaltic melt in error limits. At the same time is shown, that about 30 % Fe^{3+} is reduced up to Fe^{2+} in glass after "long" runs by duration up to 120–130 minutes at pressure 5 kbar with initial oxidised basaltic glass ($\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+}) = 0.8$). In these reduced samples ($\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+}) \approx 0.5$) the FTIR-spectroscopy detects the significantly higher concentrations of H_2O (0.5–0.7 wt. %) on a comparison with H_2O concentrations in initial glass and quench glasses after "short" experiments (0.05–0.15 wt. % H_2O). Because of it is supposed, that the main reason of partial reduction of Fe^{3+} in "long" runs is the hydrogen penetration in a basaltic melt through platinum walls of the capsule from surrounding gas medium during experiment. The obtained data give the serious basis to doubt, that a pressure increase till 5–10 kbar can to cause strong reduction effect (decrease of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio) in synthetic and natural silicate melts (in closed system conditions), discovered earlier in experiments conducted mainly on the piston-cylinder high pressure apparatus [1–5].

The study of Mössbauer spectra of experimental glass samples with an identical iron redox state allows to conclude, that the pressure variation in range up to 5 kbar does not produce noticeable influence to

a structural positions Fe^{3+} and Fe^{2+} in basaltic melts. There is the monomodal distribution of isomeric shift value for each from iron ions in all experimental samples, in other words there is the quasicontinuous distribution of lengths of Fe-O bindings in a near coordination sphere. Thus, in a structure of a glass (melt) for each from iron ions there are no two (or more) preferable structural positions, which would be strictly attribute to tetrahedral and/or octahedral coordination. Obviously, it is possible to speak only about some effective coordination number for each from them. Effective coordination number of Fe^{3+} is inside the range between 5 and 6. It is close to 5 in oxidised glasses (melts) with a ratio $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+}) \approx 0.8$ and increases with decrease of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. Effective coordination number of Fe^{3+} comes close to 6 (deformed octahedron) at $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+}) \approx 0.5$. Effective coordination number of Fe^{2+} is between 4 and 5.

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