

Structural role of Fe in a peralkaline silicate melt

Karl Thomas Fehr,¹ Gabriele Giuli,² Kai-Uwe Hess,¹ Donald B. Dingwell,¹ Paola Valenti,³ Eleonora Paris,²

1 Department of Earth and Environmental Sciences, Ludwig Maximilians Universität, Theresienstr. 41/III, 80333 Munich, Germany

2 School of Science and Technology, Geology Division, University of Camerino, Via Gentile III da Varano, 62032 Camerino, Italy

3 GeoForschungsZentrum, Potsdam, Telegrafenberg, 14473 Potsdam Germany

Iron in silicate melts can play a variety of structural roles involving different coordination numbers and oxidation states. Common Fe species in the melt include $^{[4]}\text{Fe}^{2+}$, $^{[5]}\text{Fe}^{2+}$, $^{[4]}\text{Fe}^{3+}$, and $^{[5]}\text{Fe}^{3+}$. The relative proportions between these species can vary considerably according to bulk glass composition and oxygen fugacity conditions. However, in most natural and synthetic silicate glasses [4]- and [5]-fold coordinated Fe^{2+} , and [4]-fold coordinated Fe^{3+} are the most common Fe species. Being a major element in silicate melts, Fe can affect considerably important physical properties like density and viscosity of a magma. Moreover, even at constant bulk composition and Fe content, also the Fe oxidation state is known to affect the melt viscosity.

In order to study the Fe structural role in peralkaline silicate melts and its effect on their viscosity, a set of silicate glasses with phonolitic composition have been synthesized at different oxygen fugacity conditions (ranging from air down to IW buffer). These glasses have been previously characterized by titration to get the Fe oxidation state. Moreover, the viscosity has been measured for each glass/melt at different temperatures. In addition the local environment of Fe was determined by XAS (Giuli et al., 2011). During the course of this study the glasses were analyzed by ^{57}Fe Moessbauer spectroscopy (MB). The spectra were taken at 298K in transmission mode and fitted by applying an extended Voigt-based lineshape according to Botcharnikov et al., 2005. The MB spectra of all samples display three lines which can be described to two different doublets. One doublet with an isomer shift (δ) of ca. 0.9 mm/s relative α -iron and a quadrupole splitting (ΔE_Q) of ca. 2 mm/s can be attributed to ferrous iron. The second doublet with δ of ca. 0.3 mm/s relative α -iron and ΔE_Q of ca. 0.9 mm/s can be attributed to ferric iron. The later values are close to that of ferric iron on tetrahedral site in ferrobasaltic glasses (Botcharnikov et al., 2005). With increasing oxidation the ΔE_Q of ferric iron increases slightly from 0.85 mm/s ($0.3 \text{ Fe}^{3+}/\text{Fe}_{\text{total}}$) to 0.95 mm/s ($0.8 \text{ Fe}^{3+}/\text{Fe}_{\text{total}}$) in contrast to ferrobasaltic glasses where a decrease of ΔE_Q for ferric iron as a function of oxidation was observed. The δ of 0.9 mm/s for ferrous iron remains constant up to an oxidation state of $0.6 \text{ Fe}^{3+}/\text{Fe}_{\text{total}}$ and with increasing oxidation a rapid decrease to δ of 0.6 mm/s at $0.8 \text{ Fe}^{3+}/\text{Fe}_{\text{total}}$ occurs. At the oxidation state of $0.6 \text{ Fe}^{3+}/\text{Fe}_{\text{total}}$ the constant ΔE_Q of 2.0 mm/s for ferrous iron increase up to 2.45 mm/s at $0.8 \text{ Fe}^{3+}/\text{Fe}_{\text{total}}$ in contrast to ferrobasaltic glasses, where a ΔE_Q of 2.0 mm/s remains constant over the whole oxidation state (Botcharnikov et al., 2005). In allusion to tektites the doublet with δ of 0.9 mm/s and 0.6 mm/s can be attributed to ferrous iron on a five-fold and four-fold coordinated sites, respectively (Rossano et al., 1999). These observations and the calculated ferric/ferrous ratios are in accordance with the XAS data of Giuli et al., 2011.

References

Botcharnikov, RE; Koepke, J; Holtz, F; McCammon, C. & Wilke, M (2005). GCA 69, 5071-5085

Giuli, G; Paris, E; Hess, K-U; Dingwell, DB; Cicconi, RM; Eeckhout, SG; Fehr, KT & Valenti, P
(2011) Amer.Miner. 96, 631-636
Rossano, S; Balan, E; Morin, G; Bauer, J-P; calas, G & Brouder, C (1999) PCM 26, 530-538