SHORT-RANGE STRUCTURE OF IRON IN ANORTHITE-DIOPSIDE GLASS

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Iron is the dominant transition element in natural glasses and melts; hence an understanding of its structural behaviour is of primary importance to knowledge of physical properties such as density and viscosity, chemical properties such as redox behaviour, and dynamic processes such as magma generation and volcanism. Mössbauer spectroscopy provides a measure of the short-range structure of iron in glass, as well as a quantitative determination of $Fe^{3+}/\Sigma Fe$, which can provide information on the T-fO_2 history of natural magmas. However Mössbauer spectra reflect site-to-site distortions of iron coordination polyhedra which complicate spectral analysis. Various approaches have been suggested, and while $Fe^{3+}/\Sigma Fe$ is relatively independent of the fitting method, the hyperfine parameters that relate to the short-range structure of iron are generally not. We therefore undertook a study of a well characterised suite of glasses in order to develop a fitting approach that could be applied over a wide range of iron compositions (both Fe^{2+} and Fe^{3+}), with the goal of characterising the effect of oxygen fugacity and glass composition on the short-range structure of iron in these glasses.

The glasses comprised two series: (1) 1 wt% $^{57}Fe_2O_3$ added to $An_{42}Di_{58}$ (nominally corresponding to the eutectic composition) and equilibrated at 1409°C over a range of oxygen fugacities from $fO_2 \sim 10^5$ bars ($Fe^{3+}/\Sigma Fe=1$) to 10^{-13} bars ($Fe^{3+}/\Sigma Fe=0$); (2) increasing amounts of Fe_2O_3 (2, 4, 7, 10, 20 or 30 wt%) added to the same $An_{42}Di_{58}$ starting composition and equilibrated at 1409 °C and three different oxygen fugacities (10^0, 10^{-4} and 10^{-7} bars). The glasses were studied using XANES (BERRY et al., 2003) where Fe^{3+} concentrations were calibrated based on Mössbauer analysis using a multiple Lorentzian doublet approach (JAYASURIYA et al., 2004). The derived Fe^{3+}/Fe^{2+} values are proportional to $\log fO_2$ with a slope of 0.245±0.004, in excellent agreement with the theoretical value of 0.25 predicted by thermodynamics (JAYASURIYA ET AL., 2004). The present study evaluates the degree to which structural information can be extracted from the Mössbauer data, and shows that an extended Voigt-based fitting analysis with two-dimensional distributions of isomer shift and quadrupole splitting reveals significant trends in the dataset, including the presence of four- and five-fold coordinated Fe^{2+} Variations in the structural state of iron as a function of oxygen fugacity and total iron concentration provide insight into the physical and chemical properties of the corresponding silicate melts.

References
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