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A Mössbauer study of the oxidation state of Fe in silicate melts

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ABSTRACT

$Fe^{3+}/\Sigma Fe$ ratios were determined from Mössbauer spectra recorded for a series of 17 anorthite-diopside eutectic glasses containing 1 wt% $^{57}Fe_2O_3$ quenched from melts equilibrated over a range of oxygen fugacities from $f_{O_2} \sim 10^5$ bars ($Fe^{3+}/\Sigma Fe = 1$) to 10^{-13} bars ($Fe^{3+}/\Sigma Fe = 0$) at 1682 K. Fe^{3+}/Fe^{2+} was found to be proportional to f_{O_2} to the power of 0.245 ± 0.004, in excellent agreement with the theoretical value of 0.25 expected from the stoichiometry of the reaction $Fe^{2+}O + 0.25\ O_2 = Fe^{3+}O_{1.5}$. The uncertainty in the $Fe^{3+}/\Sigma Fe$ ratios determined by Mössbauer spectroscopy was estimated as ± 0.01 (1σ) from the fit of the data to the theoretical expression, which is significantly less than that quoted for previous measurements on silicate glasses; this results from fitting the spectra of a large number of systematically varying samples, which allows many of the ambiguities associated with the fitting procedure to be minimized. $Fe^{3+}/\Sigma Fe$ ratios were then determined for samples of the anorthite-diopside eutectic composition equilibrated at selected values of f_{O_2}, to which up to 30 wt% Fe_2O_3 had been added. $Fe^{3+}/\Sigma Fe$ was found to vary with ΣFe (or FeO_T), but both the 1 wt% and high FeO_T data could be satisfactorily fit assuming the ideal stoichiometry (i.e., $Fe^{3+}/Fe^{2+} \propto f_{O_2}{}^{1/4}$) by the inclusion of a Margules term describing Fe^{2+}-Fe^{3+} interactions. The large negative value of this term indicates a tendency toward the formation of Fe^{2+}-Fe^{3+} complexes in the melt. The resulting expression, using the ideal exponent of 0.25, gave a fit to 289 $Fe^{3+}/\Sigma Fe$ values, compiled from various literature sources, of similar quality as previous empirical models which found an exponent of ~0.20. Although the empirical models reproduce $Fe^{3+}/\Sigma Fe$ values of glasses with high FeO_T reasonably well, they describe the data for 1 wt% FeO_T poorly. The non-ideal values of the exponent describing the dependence of $Fe^{3+}/\Sigma Fe$ on f_{O_2} at high FeO_T are an artifact of models that did not include a term explicitly to describe the Fe^{2+}-Fe^{3+} interactions. An alternative model in which Fe in the silicate melt is described in terms of three species, $Fe^{2+}O$, $Fe^{3+}O_{1.5}$, and the non-integral valence species $Fe^{2.6+}O_{1.3}$, was also tested with promising results. However, at present there is no model that fits the data within the assessed accuracy of the experimental measurements.