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

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ABSTRACT

Fe3+/ΣFe ratios were determined from Mössbauer spectra recorded for a series of 17 anorthite-diopside eutectic glasses containing 1 wt% FeO, quenched from melts equilibrated over a range of oxygen fugacities from fO2 ~ 106 bars (Fe3+/ΣFe = 1) to 1011 bars (Fe3+/ΣFe = 0) at 1682 K. Fe3+/Fe2+ was found to be proportional to fO2, 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 Fe2+O + 0.25 O2 = Fe3+O1.5. The uncertainty in the Fe3+/ΣFe 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. Fe3+/ΣFe ratios were then determined for samples of the anorthite-diopside eutectic composition equilibrated at selected values of fO2, to which up to 30 wt% FeO had been added. Fe3+/ΣFe was found to vary with ΣFe (or FeO), but both the 1 wt% and high FeO data could be satisfactorily fit assuming the ideal stoichiometry (i.e., Fe3+/Fe2+ = fO21/4) by the inclusion of a Margules term describing Fe2+-Fe3+ interactions. The large negative value of this term indicates a tendency toward the formation of Fe2+-Fe3+ complexes in the melt. The resulting expression, using the ideal exponent of 0.25, gave a fit to 289 Fe3+/ΣFe 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 Fe3+/ΣFe values of glasses with high FeO reasonably well, they describe the data for 1 wt% FeO poorly. The non-ideal values of the exponent describing the dependence of Fe3+/ΣFe on fO2 at high FeO are an artifact of models that did not include a term explicitly to describe the Fe2+-Fe3+ interactions. An alternative model in which Fe in the silicate melt is described in terms of three species, FeO+, FeO1.5, and the non-integral valence species Fe2.6+O1.3, 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.

INTRODUCTION

In most terrestrial magmas, Fe is overwhelmingly the most abundant element occurring in more than one oxidation state, namely as Fe2+ and Fe3+. The ratio of these oxidation states (conveniently described as Fe3+ΣFe) varies widely in different magma types (Carmichael 1991), and is well known to influence many of the physical and chemical properties of the magma, such as melt structure and viscosity. The Fe3+ΣFe ratio is one factor determining the temperature and composition of crystallizing phases. Due to the high abundance of Fe relative to other redox-variable elements, the Fe3+ΣFe ratio should control the oxygen fugacity (fO2) of a magma, and therefore the valencies of heterovalent trace elements and the speciation of volatile components.

The Fe3+ΣFe ratio is related to the oxygen fugacity by the reaction:

Fe2+O + 1/4 O2 = Fe3+O1.5

silicate melt

silicate melt

(1)

The stoichiometry of this relationship predicts that Fe3+ΣFe is proportional to fO2, to the power of 0.25 (Kennedy 1948); this relationship was verified experimentally by Johnston (1964) for dilute concentrations of FeO (where FeO = Fe2+O + Fe3+O3). (~2 wt%) in Na2O-2SiO2 melts. However, subsequent experimental studies on geologically relevant melt compositions have repeatedly returned significantly lower values of this exponent. Fadali (1965) found exponents that ranged from 0.16 to 0.27 for the different melt compositions that he studied, with a tendency to cluster around 0.20. Sack et al. (1980) and subsequently Kilinc et al. (1983) both reported an exponent of 0.22 from a global fit to a simplified thermodynamic formulation of Equation 1. Their input data covered a large range of compositions appropriate to natural magmas, including both their own experimental data and previous work. Subsequent refitting by Kress and Carmichael (1991) with still more data lowered the apparent exponent to 0.20. Borisov and Shapkin (1990) refitted essentially the same data as...