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Accurate determination of $Fe^{3+}/\Sigma Fe$ of andesitic glass by Mössbauer spectroscopy

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ABSTRACT

To evaluate the accuracy of Fe^{3+} and Fe^{2+} ratios in silicate glasses determined by Mössbauer spectroscopy, we examine in detail the temperature (47–293 K) of Mössbauer spectra for two andesitic glasses, one quenched at 1 atm, 1400 °C (VF3) and the other at 3.5 GPa, 1600 °C (M544). Variable-temperature Mössbauer spectra of these two glasses are used to characterize the recoilless fraction, f, by two different methods—a relative method (RM) based on the temperature dependence of the ratios of Fe^{3+} and Fe^{2+} Mössbauer doublets and the second based on the temperature dependence of the center shift (CS) of the doublets. The ratio of the recoilless fractions for Fe^{3+} and Fe^{2+}, C_T, can then be used to adjust the observed area of the Mössbauer doublets into the $Fe^{3+}/\Sigma Fe$ ratio in the sample. We also evaluated the contributions of non-paramagnetic components to the Fe in the glasses by determining the influence of applied magnetic field on sample magnetization. Finally, for the VF3 glass, we determined the $Fe^{3+}/\Sigma Fe$ independently by wet chemical determination of the FeO content combined with careful electron microprobe analyses of total Fe. Recoilless fractions determined with the CS method (CSM) are significantly smaller than those determined with the relative method and suggest larger corrections to room-temperature $Fe^{3+}/\Sigma Fe$ ratios. However, the RM determinations are believed to be more accurate because they depend less on the assumption of the Debye harmonic model and because they produce more nearly temperature-independent estimates of $Fe^{3+}/\Sigma Fe$ ratios. Non-linear responses of sample magnetizations to applied magnetic fields indicate that the glasses contain a small (0.4–1.1% for VF3) superparamagnetic component that is most likely to be nanophase precipitates of $(Fe,Mg)Fe_2O_4$ oxide, but corrections for this component have negligible influence on the total $Fe^{3+}/\Sigma Fe$ determined for the glass. For the VF3 glass, the $Fe^{3+}/\Sigma Fe$ produced by uncorrected room-temperature Mössbauer spectroscopy [0.685 ± 0.014 in two standard deviation (2σ)] agrees within 3% of that determined by wet chemistry (0.666 ± 0.030 in 2σ). The $Fe^{3+}/\Sigma Fe$ corrected for recoilless fraction contributions is $0.634 \pm 0.078(2\sigma)$, which is 7.5% lower than the uncorrected room-temperature ratio, but also agrees within 5% of wet chemical ratio. At least for this andesitic glass, the room-temperature determination of $Fe^{3+}/\Sigma Fe$ is accurate within analytical uncertainty, but room-temperature Mössbauer determinations of $Fe^{3+}/\Sigma Fe$ are always systematically higher compared to recoilless-fraction corrected ratios.

Keywords: Mössbauer spectroscopy, silicate glass, recoilless fraction, $Fe^{3+}/\Sigma Fe$