

High-temperature Mössbauer spectroscopy: A probe for the relaxation time of Fe species in silicate melts and glasses

CORALIE WEIGEL,* CATHERINE MCCAMMON, AND HANS KEPPLER

Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

ABSTRACT

The Mössbauer spectra of an albite glass and melt doped with ^{57}Fe (bulk composition $\text{NaFe}_{0.04}\text{AlSi}_3\text{O}_8$) were measured in situ to 1100 °C. A specially designed furnace was used where a disk of the sample was enclosed in a capsule of graphite. The furnace was purged with argon to avoid oxidation of the graphite, and shields of boron nitride (BN) were used to protect both the γ -ray source and the detector from thermal radiation. Room-temperature spectra show contributions from paramagnetic Fe^{2+} , paramagnetic Fe^{3+} , and magnetic Fe^{3+} . The signal of Fe^{2+} disappears around 400 °C, and the signal of Fe^{3+} disappears at about 1100 °C. This behavior cannot be due to changes in the oxidation state of iron because in situ visible and near infrared spectra of the same sample show that Fe^{2+} persists to at least 1000 °C and the quenched samples do not show any change in oxidation state. Rather, the disappearance of Fe^{2+} and Fe^{3+} in the spectra is likely due to the structural relaxation time around these cations becoming comparable to the Mössbauer timescale (lifetime of excited state $\approx 10^{-8}$ s). We show that the temperature at which the Fe^{3+} contribution disappears corresponds to the expected glass transition temperature of a “ferrialbite” $\text{NaFeSi}_3\text{O}_8$ melt for a timescale of 10^{-8} s. Our data therefore confirm that viscous flow is due to the rearrangement of the chemical bonds between oxygen anions and network-forming cations. Furthermore, our data show that Mössbauer spectroscopy can be used to study the speciation and relaxation time around iron in silicate melts even at temperatures above the macroscopic glass transition temperature as defined from viscosimetry and calorimetry.

Keywords: Glass transition, iron, Mössbauer spectroscopy, silicate glasses, structural relaxation, relaxation time