American Mineralogist, Volume 83, pages 1022–1029, 1998

Structure and dynamics of magnesium in silicate melts: A high-temperature ^{25}Mg NMR study

Anna M. George and Jonathan F. Stebbins*

Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305, U.S.A.

Abstract

^{25}Mg NMR spectra for several silicate and aluminosilicate melts were obtained from 1000–1470 °C. The peaks are initially very broad, but narrow with increasing temperature to near 500 Hz at the highest temperatures. The peak positions for most of the melts do not shift noticeably with temperature in the range studied, except for a sodium magnesium silicate composition that was previously studied by Fiske and Stebbins (1994). This material showed a decrease in frequency of the peak position by about 4 ppm between 1150–1360 °C in both this and the previous study, consistent with an increase in the average size of the site. The chemical shifts vary with composition as well, ranging from 31 ppm for a potassium sodium magnesium silicate melt to 22 ppm for diopside melt ($CaMgSi_2O_6$) at 1400 °C. Compositions with higher field strength cations have lower frequency chemical shifts, which correspond to larger coordination numbers and bond lengths for Mg^{2+}. All of the peak positions obtained fall to slightly higher frequency than the range for sixfold-coordinated Mg in crystals and well below the fourfold-coordinated range, indicating that the Mg is in fivefold to sixfold coordination in the melts. Spin-lattice relaxation times show that measurements are on the high-temperature side of the T_1 minima, and a simple expression for quadrupolar relaxation can be used to obtain correlation times for the motion responsible for the relaxation. The correlation times obtained in this manner are very similar to the correlation time τ_{shear} obtained from viscosity measurements, implying that the Mg motion is strongly coupled to the network motion at these temperatures. Line widths also scale with T_1 in this temperature range, leading to the conclusion that the viscosity is the fundamental limit to observing the ^{25}Mg signal in the melt.