Probing the degree of polymerization in iron-bearing calcium silicate glasses: A view from high-resolution solid-state Nuclear Magnetic Resonance

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Abstract

Unveiling the atomic structure of iron-bearing silicate glasses is one of the fundamental unsolved problems in glass sciences and high-temperature geochemistry. Whereas solid-state NMR has been effective in probing the local structures of iron-free oxide glasses, its application to the study of iron-bearing glasses has been limited due to the considerable peak broadening and signal loss stemming from paramagnetic effect. Nevertheless, a recent NMR study demonstrated the utility of solid-state NMR techniques, such as 2-dimensional MQ-MAS (multiple-quantum magic-angle spinning) for the study of structure of iron-bearing Na-silicate glasses [1]. While this progress holds strong promise for study of hidden structural details in diverse iron-bearing oxide glasses, the previous analyses are rather qualitative and the quantification of the degree of melt polymerization in the iron-bearing glasses has remained to be performed. Here, we report the extent of polymerization in iron-bearing calcium silicate glasses (CaO-Fe2O3-SiO2) with varying XFe2O3 [=Fe2O3/(CaO + Fe2O3)], up to 12.9 wt% Fe2O3). The 29Si NMR spectra show an apparent increase in highly polymerized Q species with increasing XFe2O3, suggesting an increase in the degree of polymerization. 17O 1D MAS NMR spectra presented the well-resolved bridging oxygen (BO, Si-O-Si) and non-bridging oxygen (NBO) peaks. The latter decreases with increasing XFe2O3, consistent with the 29Si NMR results. Despite the severe peak broadening, the iron-induced changes in the structurally-relevant NMR parameters, such as isotropic chemical shift (δiso) and quadrupolar coupling constant (Cq) were estimated from 17O 2D 3QMAS NMR spectra for the iron-bearing Ca-silicate glasses. The results reveal that the paramagnetic effect results in a more pronounced dispersion of δiso, while its effect on Cq is effectively suppressed. Together with our earlier NMR studies of iron-bearing Na- and Mg silicate glasses [1,2], we established the systematic effects of paramagnetic elements and cation field strength of non-framework cations on NMR peak shift and broadening.

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