Magic-Angle Spinning spectroscopic imaging of chemical composition gradients in bulk glass samples

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Résumé

While multiple studies have investigated the dynamics of diffusing species in silicate melts, we have little understanding of the local structural changes occurring across concentration gradients. Solid-state NMR has proven to be a powerful tool to study the local range order in glasses. It requires the material to be ground, however, limiting its use for samples exhibiting spatially-dependent properties. This limitation can now be overcome by taking advantage of modern NMR imaging capacities. In this work, we successfully performed 23Na, 27Al and 29Si Magic-Angle Spinning (MAS) chemical shift imaging of composition gradients in a bulk glass piece. The sample was prepared by inter-diffusion at 1200∘C of two Na2O-CaO-Al2O3-SiO2 glass pieces exhibiting 5 wt% differences in Na2O and Al2O3 content. The resulting concentration gradients spanned over distances of up to 2 mm on each side of the interface for the most mobile species, typically Na and Ca. The glass sample was scanned across a height of approximately 6 mm and spatial resolutions below 100 μm were achieved with all nuclei, ensuring proper resolution of the signal evolution between the two glass media. This allowed to probe the structure along the specific features described by electron microprobe concentration profiles. We show that 23Na and 27Al chemical shift profiles are highly correlated and follow the trend of the glass Na content. This observation is consistent with Na preferentially adopting a charge-balancing role in the vicinity of AlO4- tetrahedra in aluminosilicate glasses. The imaging data was also compared to spectral acquisitions on the end-member glasses and a synthesized glass of the interface composition. The comparison shows that the structure at different positions on the concentration profiles is the same as that of a glass of equivalent composition. Taking that into consideration, imaging profiles of samples exhibiting gradients of local environments could be used to characterize a whole sample set in a single experiment.

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