Detection of “Free” Oxide Ions in Silicate Glasses by Double-Resonance Solid-State NMR

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Knowledge of the molecular-scale structure of oxide glasses and glass-forming liquids is of key importance in understanding, predicting, and optimizing their physical and chemical properties for applications to both advanced technological materials and to basic research in the Earth sciences. Of particular importance is the role of the oxygen anion, which is numerically and volumetrically predominant in all oxide glasses, and connects the Si cations to define the glass ‘network’.

In conventional models of most glass-forming compositions, all oxide ions should be bonded to one or two network cations such as Si^{4+}, but recent studies by NMR and other methods have suggested this view may need revision and that “free” oxide ions may play an important role. This controversy has proven difficult to resolve.

We present a technically-challenging double-resonance NMR experiment involving ^{17}O and ^{29}Si that quantifies ‘free’ oxide O^{2-} species in $CaMgSiO_4$ glasses. The technique, called CP-HETCOR, measures the transfer of nuclear spin polarization between oxygen and silicon atoms. Isotopic enrichment, special methods to form low-silica glasses, NMR pulse sequence development, testing with crystalline model compounds of known structure, and high magnetic fields are all required to make this measurement possible.[1]

Facilities: NMR facility at NHMFL, 800 Mhz MB

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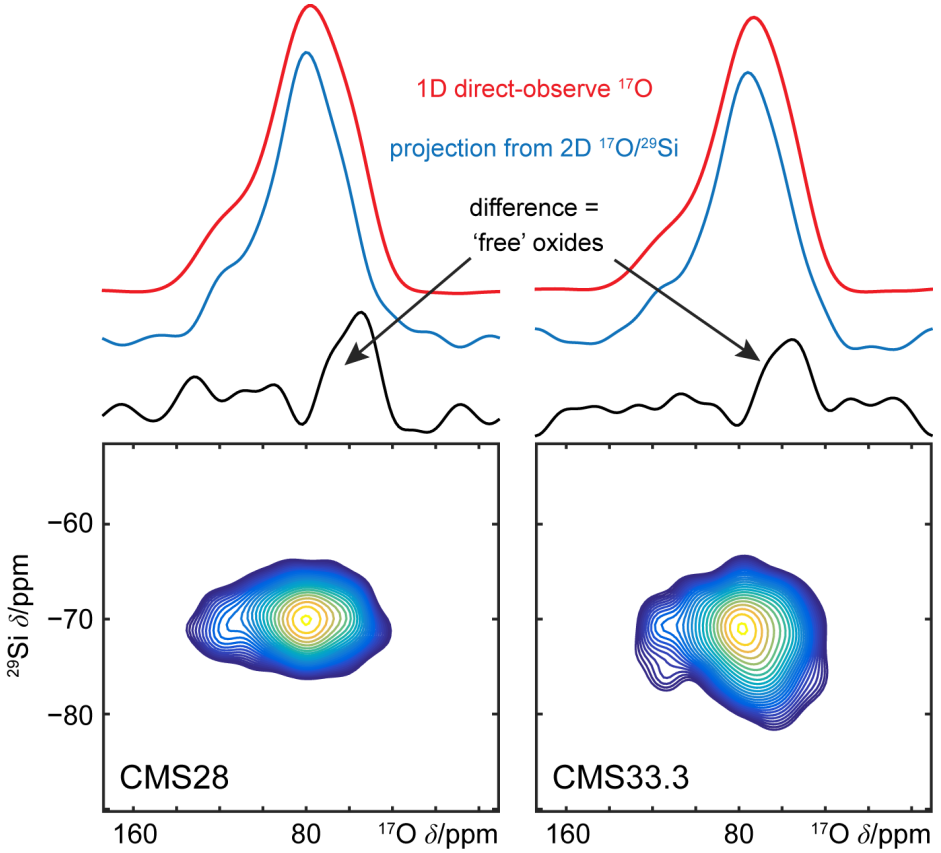

Comparison of 2D $^{17}O \rightarrow {}^{29}Si$ CP HETCOR projections (blue) with directly measured ^{17}O magic angle spinning NMR spectra (red). The difference spectra (black) shows the signal for oxide ion sites that have *no* direct silicon neighbors, thus the ‘free’ oxide ion. The chemical shift of this signal confirms that it is due to O^{2-} with only Mg^{2+} cation(s) as its first nearest neighbors.