Goldschmidt Medal Abstract

NMR Measurements on Aqueous Electrolyte Solutions to 2.0 GPa

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Even an oxide ion with 40 atoms captures much of the macroscopic chemistry of mineral-fluid reaction kinetics--isotope-exchange and dissociation reaction pathways involve concerted motions of many atoms, amphoteric chemistry and metastable states[1]. All of these insights were gained via solution NMR spectroscopy and tagged experimental models. High-pressure NMR spectroscopy is particularly useful because it can detect changes in reaction volumes as are caused by altered solvation states. Recent advances in the simulation of aqueous solutions has also estimated dielectric constants of water to 6.0 GPa and 1200ºC, well beyond the previous limits (<0.5 GPa)[2].

Thus we designed an NMR probe[3] that allows experiments to 2.0 GPa and is so simple that it can be used by students. The probe involves a microcoil solenoid in a clamped-cell device, with temperature control, multinuclear circuitry and a sample volume of 0.01-0.02 mL. Pressures are estimated by a ruby sphere glued to a fiberoptic cable and periodically coupled to a spectrometer that reads the fluoresence signal. Pressure is increased intermittently using a simple hydraulic ram.

We here show ^{11}B, ^{2}H, ^{139}La and ^{133}Cs spectra collected at pressures of up to 1.8 GPa, where the hydrogen-bonded structure of water has largely collapsed and nuclear relaxation is dominated by solution viscosities. These can be measured *in situ* using magnetic-field gradients to estimate the diffusion coefficients and thus the viscosities via the Stokes-Einstein relation. Freezing of the electrolyte solutions is kinetically slow and suppressed by the solutes so that NMR measurements can be made in metastable solutions at nearly twice (<1.8 GPa) the nominal freezing pressure (0.9 GPa), providing information about solution chemistry well beyond where it was anticipated to be inaccessible.

[1] Rustad, J. R. and Casey, W. H. (2012) *Nature Materials* **11**, 223-225. [2] D. Pan et al., *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 6646. [3] Pautler, et al., (2014) *Angewandte Chemie* **53**, 9788-9791; Ochoa, G. et al., (2015) *Angewandte Chemie* **54,** 15444-15447.