

## Solution-state NMR spectroscopy up to 20 kilobars

B.G. PAUTLER<sup>1\*</sup>, C.A. COLLA<sup>2</sup>, R.L. JOHNSON<sup>1</sup>,  
P. KLAVINS<sup>3</sup>, S.J. HARLEY<sup>4</sup>, C.A. OHLIN<sup>5</sup>  
AND W.H. CASEY<sup>1,2</sup>

<sup>1</sup>Department of Chemistry, UC Davis, USA

<sup>2</sup>Department of Earth and Planetary Sciences, UC Davis, USA

<sup>3</sup>Department of Physics, UC Davis, USA

<sup>4</sup>Energetic Material Division, Lawrence Livermore National  
Laboratory, USA

<sup>5</sup>School of Chemistry, Monash University, Australia

The reactivity of elements in nature is among the most pressing concerns in environmental geochemistry. Simple reactions, such as ligand exchange, are often probed via activation volumes which yield information about changes in solvation in the transition states. Activation volumes derived from pressure-dependencies of reaction rates have been successfully measured by solution-state <sup>13</sup>C, <sup>31</sup>P, and <sup>17</sup>O NMR on uranyl-containing complexes up to 3.5 kbar, which is the current practical limit of such measurement.<sup>1-2</sup> A nonmagnetic piston-cylinder pressure cell has been developed for solution-state NMR applications to measure pressure dependencies of a wide variety of NMR-active nuclei up to 20 kbar with as little as 10  $\mu$ L of sample contained within an NMR micro-coil. Using a fibre-optic measurement technique, the pressure inside the piston cylinder has been calibrated via *in situ* ruby fluorescence.<sup>3</sup>

Initial <sup>11</sup>B NMR investigations on simple organic ligand - boron complexes up to 8 kbar reveals a pH dependent dynamic exchange processes as a function of pressure that are fitted to site-exchange models to extract chemical kinetic and equilibrium constants. A solution containing boric acid and catechol in equilibrium at pH 5 initially shows three distinct <sup>11</sup>B chemical environments, corresponding to free boric acid, borate-catechol mono and diols in equilibrium that broaden and coalesce at 8 kbar, suggesting fast equilibrium exchange between the species in solutions likely the result of the pressure dependences on the pKa of borate.

This technique was extended to examine silica speciation by <sup>29</sup>Si NMR and preliminary results suggest a change in coordination as a function of pressure. The success of these high-pressure solution NMR experiments suggests this probe design can be applied to a wide variety of NMR active nuclei in aqueous solutions.

[1] Johnson *et al* (2013) *Angew. Chem. Int. Ed.*, **52**, 7464-7467

[2] Harley *et al* (2011) *Angew. Chem. Int. Ed.* **50**, 4467-4469

[3] Koyama-Nakazawa *et al* (2007) *Rev. Sci. Instrum.* **78**, 066109 (3pp)