Boron speciation and isotope systematics in seawater, biological and inorganic carbonates

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The unique set of geochemical characteristics of the boron isotope system in seawater and marine biological carbonates makes it appealing for paleo-pH reconstructions. First, pH dependent equilibration of boric acid B $(OH)_3^o$ and borate anion B $(OH)_4^-$ in seawater is accompanied by a large isotope fractionation, i.e. 27.2 ‰ [1]. Second, $\delta^{11}B$ in marine carbonates suggests the predominant uptake of borate anion [2]. However, the recent discovery of both BO_3^- and BO_4^- coordinated structures in almost equal abundances in biogenic calcite and aragonite specimens [3] points to subtleties in biologically mediated boron uptake, which have yet to be clearly resolved. Added complexity comes from the vital effects on $\delta^{11}B$ of marine calcifiers associated with a variable pH at the site of calcification, which is currently the area of active research [4].

We carried out a series of pH-controlled precipitation experiments of inorganic calcite and aragonite at 25°C in order to isolate purely abiological effects on carbonate $\delta^{11}B$ during calcium carbonate precipitation from NaCl solutions (I~0.7) in the presence of borate species. Our preliminary results from aragonite precipitates at pH~8.7 are in excellent agreement with the $\delta^{11}B$ value for aqueous borate predicted by 27.2 ‰ fractionation. Further experiments will focus on the investigation of boron partitioning into inorganic carbonates at lower pH ranges.

[1] Klochko *et al.* (2006) *EPSL* **248**, 261–270. [2] Hemming & Hanson (1992) *GCA* **59**, 371–379. [3] Klochko *et al.* (2009) *GCA* **73**, 1890–1900. [4] Rollion-Bard & Erez (2010) *GCA* **74**, 1530–1536.

Advances in high pressure neutron scattering

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High pressure is a window to view matter in unusual states. In this talk I will show what neutron scattering is able to contribute to a better understanding of matter under pressures in the 0-30 GPa range. I will discuss the considerable efforts made recently by various groups to extend the capabilities of high-pressure neutron scattering, i.e. to achieve higher pressures and better data quality, and to make it available to a broad scientific community. The methods involved are all based on opposed-anvil techniques which allow sample volumes of up to 100 mm^3. I will illustrate these advances on two examples covering molecular systems under high pressure investigated by methods which apply the so-called 'Paris-Edinburgh' high pressure technique: ice and solid oxygen.

In a recent studies we investigated the behaviour of glassy solutions of $LiCl6H_2O$ under pressure and discovered very unusual recrystallisation behaviour [1]. When this system is compressed a low temperatures to 4 GPa it recrystallizes at ~ 270 K into ice VII which incorporates Li and Cl into its structure. This form of 'salty ice VII' has unusual structural and dynamical properties, such as a 8% larger unit cell volume, exceptionally large displacement factors and 'plasticity', i e. a rotational dynamcis which is governed by hte diffusion of Li. This obeservations may have implications on modelling icy bodies of the outer solar system. The second example covers magnetism in solid oxygen under high pressure. Oxygen is the only elemntal molecule which carries a mangetic moment, and is hence able to show magnetic ordering in its solid form. In recent work we investigated solid oxygen up to pressures of 8 GPa and discovered a complex magnetic phase diagram in its 'orange phase', i.e. δ-O_2 [2]. We demonstrate the existence of three different antiferromagnetic structures between 20 and 240 K. This example is a perfect illustration of the power of high pressure neutron scattering to study magnetism and structure simultaniously, as well their mutual interplay.

[1] S. Klotz, L. Bove, Th. Strässle, Th. Hansen, A.M. Saitta, (2009) *Nature Materials* **8**, 405. [2] S. Klotz, Th. Strässle, A. Cornelius, J. Philippe, Th. Hansen, (2010) *Phys. Rev. Lett.* **104**, 115501.