# Experimental Report



**Proposal:** **6-02-502** **Council:** 4/2012

**Title:** Structure of Geological Fluids

**This proposal is a new proposal**

**Researh Area:** Other...

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**Samples:** NiCl2 in D2O, natural Ni and the isotope 62Ni

| Instrument | Req. Days | All. Days | From | To |
|---|---|---|---|---|
| D4 | 7 | 5 | 01/03/2013 | 07/03/2013 |

**Abstract:**

We propose to make the first investigation by using neutron diffraction and isotope substitution of an aqueous ionic solution at pressures beyond 0.2 GPa. The focus of attention will be on a concentrated solution of 4.41 molal NiCl2 in D2O under the same state conditions for which we have already examined the structure of pure D2O i.e. at pressures ranging from 0.1 to 2.5 GPa at a temperature of 150 deg C. Use of the first difference method will eliminate those pair correlation functions that do not involve the Ni2+ aqua-ion, along with the main contributions from inelastic scattering. The results will therefore provide the first detailed account on how the coordination environment of an aqua-ion varies over an extensive range of pressure and will have relevance for the mineral trapping of CO2. Success will lead to the possibility of investigating other aqueous ionic solutions of geochemical importance.

**Structure of Geological Fluids**

This proposal involved the first use of the method of neutron diffraction with isotope substitution (NDIS) to geologically relevant fluids in a Paris-Edinburgh press at pressures in the range 0.2 – 4 GPa and at temperatures up to 150 °C. The focus of attention was on solutions of $NiCl_2$ in $D_2O$, which have already been extensively investigated under different state conditions [1, 2]. The aim was to use Ni isotope substitution to examine in detail the changes that occur to the coordination environment of the $Ni^{2+}$ aqua ion under extreme conditions. Such experiments are extremely challenging owing to the use of small sample sizes, the small concentration of the isotopically enriched chemical species, and the large background signal associated with Paris-Edinburgh press experiments.

The isotopically enriched Ni samples were, unfortunately, lost on transportation to the ILL. We therefore attempted to apply the method of isomorphic substitution in neutron diffraction to solutions of $NiCl_2$ and $MgCl_2$ in $D_2O$ [3, 4] using samples that we made-up at the ILL. The measured intensities for the $NiCl_2$ solution at a temperature of 150 °C and at pressures in the range from 0.3 – 3.7 GPa are shown in figure 1. The intensities for the $MgCl_2$ solution are not, however, shown because the sample preparation led to an unwanted precipitate that gave Bragg peaks i.e. meaningful first-difference functions could not be constructed by combining the data sets for the $NiCl_2$ and $MgCl_2$ solutions. Nevertheless, this preliminary experiment gained vital experience and led to a successful application of the *in situ* high-pressure NDIS method with a Paris-Edinburgh press to aqueous solutions of NaCl in $D_2O$ [5].

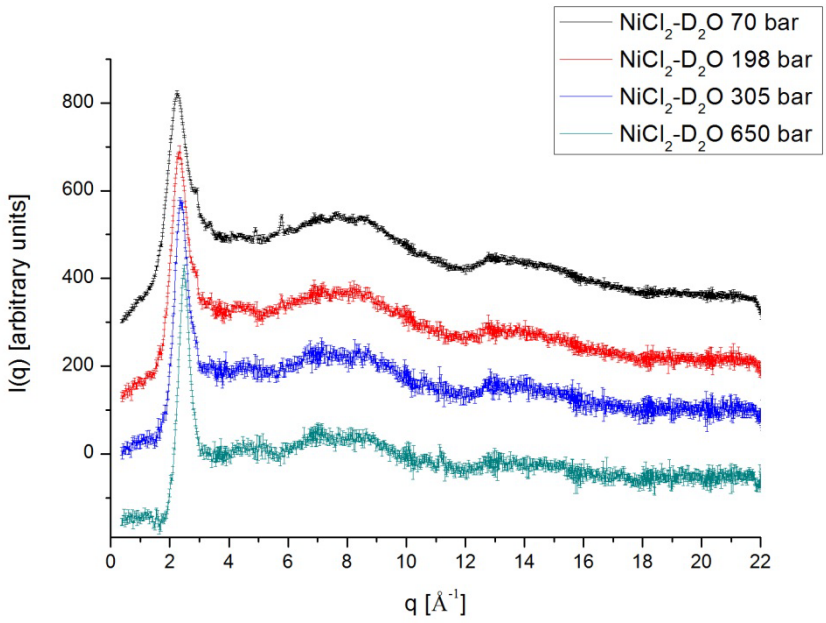


Figure 1. The background corrected intensity $I(q)$ as a function of pressure for a 4.35 molal solution of $NiCl_2$ in $D_2O$ at 150 °C as measured in a Paris-Edinburgh press. The quoted oil pressures of 70 – 650 bar correspond to sample pressures between 0.3 and 3.7 GPa.


[1] Neilson G W and Enderby J E 1983 *Proc. R. Soc. Lond. A* **390**, 353.
[2] de Jong P H K, Neilson G W and Bellissent-Funel M-C 1996 *J. Chem. Phys.* **105**, 5155
[3] Skipper N T, Cummings S, Neilson G W, Enderby J E 1986 *Nature* **321**, 52
[4] Skipper N T et al. 1989 *J. Phys.: Condens. Matter* **1**, 3489
[5] ILL report 6-02-518