Experimental Report

Proposal: **6-02-534** **Council:** 4/2014

Title: Vibrational dynamics of adsorbed water under pressure: thermodynamicsof intergranular water in geological media

This proposal is a new proposal

Researh Area: Other...

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Samples: Mg(OH)2

Instrument	Req. Days	All. Days	From	To
IN1 LAG	8	8	14/11/2014	22/11/2014

Abstract:

Water in deep-seated rocks (lower crust, subduction zones), when present, is expected to mostly occur as thin films wetting the surface of hydrophyllic minerals. Its physical and chemical properties must therefore significantly depart from those of bulk water. We propose to use incoherent inelastic neutron scattering (IINS) experiment to probe the vibrational density of states (vDOS) of water in the intergranular medium under high pressure and high temperature conditions. In parallel to these experiments, molecular dynamics simulations will be performed with the support of the ILL's C-Lab. The targeted sample is a brucite, Mg(OH)2, polycrystal which (1) exhibits dominant {100} surfaces and which (2) is subjected to water transfer (at around 700 K, 2 GPa) from bulk to intergranular region below the brucite dehydration temperature as already shown using in-situ impedance spectroscopy. In order to perform this study, we plan to use the high pressure cell available at LAGRANGE and which can be run up to pressures 2 GPa, i.e. perfectly relevant to the Earth's conditions where intergranular water properties are totally unknown .

Experimental report 6-02-534

Vibrational dynamics of adsorbed water under pressure: towards an understanding of the thermodynamics of intergranular water in geological media

Experimental team: Alejandro Fernandez-Martinez, Fabrice Brunet, Claudia Mondelli, Martin Wilding, Fabrizio Bardelli, Ravil Sadykov

Local contact: Monica Jimenez-Ruiz

Dates: 15-22 November 2014

The aim of the experiment was to measure the vibrational density of states of water adsorbed on brucite nanoparticles (~disk shaped, 10 nm thickness & 100 nm diameter) under pressure, using a piston high-pressure cell brought to the ILL by Ravil Sadykov (National Academy of Sciences, Institute of Nuclear Research, Russia).

Ambient-pressure data were taken during the first part of the experiment, using the high-pressure cell as sample-holder. Difficulties associated with the ex-situ procedure to dry the sample made that the acquisition of high-pressure data was delayed until the last days of the experiment. Obtaining good data for dry brucite is very important in order to have a good background signal we can substract from the wet brucite data. Substracted data are shown in Figure 1, bottom. The presence of a wide band between 500 and ~1300 cm^{-1} is in agreement with what is expected from librational modes of water (bulk). However, the statistics are low (error bars, not shown, are of the same order of magnitude as the noise level; a smoothing of the data is shown in a continuous red line to help visualizing the data). Other difficulties were associated with the fact that a pressure-transmitting medium (fluorinert) was used in the measurements with the high-pressure cell. The difficulty arise due to the fact that the exact mass of the sample in the high pressure cell cannot be measured with high precision if fluorinert is used, which prevents performing an accurate data normalization.

High pressure data were obtained at 11 and 15 kbar for dry and wet brucite, the last one with a water equivalent to two layers of water. However, data wet-dry substraction was not successful due to (1) low statistics and (2) inadequate dry background (sample preparation was not optimal due to the use of fluorinert).

Several points will be considered in a future high-pressure experiment in order to solve the issues indicated above:

1) Longer counting times will be used, up to 24h, so enough statistics can be accumulated (~$2*10^6$ monitor counts).
2) Brucite compressibility is quite low (~36 GPa). Experiments without a pressure transmitting medium will be performed, so the mass of the sample in the beam can be precisely quantified.
3) A sample stick allowing the in-situ drying of the brucite sample will be used. This is a fundamental point that will help acquiring data with the same background for different water contents.

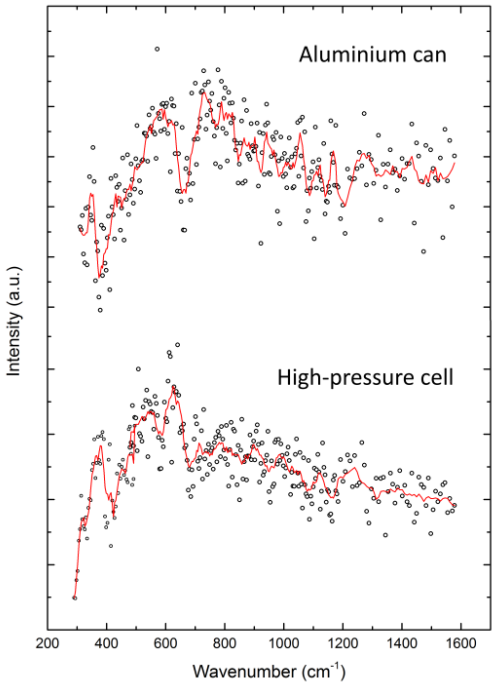

Figure 1. Left: vDOS of adsorbed water (two monolayers) at the brucite surface measured in the high pressure cell (bottom) and in the regular cell of LAGRANGE (top), obtained by doing the difference of wet and dry samples. The dots indicate the experimental points; red line is a lateral averaging of the data (5 points). Error bars are in the level of the data dispersion.