Experimental report

29/01/2016

Proposal:	**6-02-563**	**Council:**	4/2015
Title:	The role of nanoconfined H2O on the pressure-induced amorphization ofAlPO4-54*xH2O zeolite - high pressure investigation		
Research area:	Materials		

This proposal is a new proposal

Main proposer:	**Frederico ALABARSE**
Experimental team:	Frederico ALABARSE Livia BOVE
Local contacts:	Bernhard FRICK Monica JIMENEZ-RUIZ

Samples: AlPO4-54*xH2O, where X=2.17, [Al18P18O72]*39H2O

Instrument	Requested days	Allocated days	From	To
IN1 LAG	11	10	30/11/2015	06/12/2015
IN16B	8	0		

Abstract:

Here we propose to probe water diffusion together with intra- and inter-molecular vibrations in the hydrated aluminophosphate zeolite AlPO4-54*xH2O under HP (GPa). Our goal is to shed light on the role of water on pressure-induced amorphisation of the material and on possible existence of pressure-induced super-diffusion effects during water extrusion. To this aim we propose to probe the diffusive and vibrational properties of nanoconfined water in AlPO4-54*xH2O before and during its amorphization by combined QENS and IINS experiments under HP.

1st beamtime report (of two) – Proposal number: 6-02-563

The role of nanoconfined H_2O on the pressure-induced amorphization of $AlPO_4$-54*xH_2O zeolite - high pressure investigation

ALABARSE Frederico[1]; BOVE Livia[1]; FRICK Bernhard[2]; JIMENEZ-RUIZ Monica[2] and KLOTZ Stefan[1]*
[1] Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, UPMC, Paris, France
[2] Institut Laue-Langevin, Grenoble, France
*Corresponding author: alabarse@impmc.upmc.fr

Institut Laue-Langevin (ILL) doi:10.5291/ILL-DATA.6-02-563

Abstract. Due to the beamline suppression for the 3th cycle of 2015 we received a split beamtime on the hot-neutron TAS spectrometer IN1-LAGRANGE. This report presents the 1st preliminaries results about the vibrational dynamics of water molecules confined in the $AlPO_4$-54•xH_2O zeolite pores, as a function of temperature in the 172-4000 cm^{-1}range. INS spectra of $AlPO_4$-54•xH_2O were measured under low temperatures and ambient pressure conditions, inside and outside a high-pressure (HP) clamp press reaching 1.6 GPa, in order to carefully evaluate the feasibility of a quantitative high-pressure study. We successfully validated the possibility to extract the main vibrational modes of the confined water in this heavy hardware environment. INS spectra of confined water at low temperature were also compared with those of Ice Ih and low density amorphous ice (LDA).

Introduction, previous work and objectives. $AlPO_4$-54•xH_2O is a hydrated aluminophosphate with the hexagonal VFI structure (space group $P6_3$) with a=18.9678(13) Å and c=8.0997(4) Å, Z=18 [1], $[Al_{18}P_{18}O_{72}]$•$47H_2O$. This material exhibits 1-D pores along the **c** direction, which are among *the largest pores known for zeolites and aluminophosphates*, with a diameter of 12.7 Å and is, thus, an interesting target material to study nanoconfined water under high pressures and low temperatures. The framework is built up of 4, 6 and 18-membered rings of alternating AlO_6, AlO_4 and PO_4 polyhedra. One-third of the aluminium cations are octahedrally coordinate due to the presence of two H_2O molecules in their coordination sphere and additional H_2O molecules form a disordered hydrogen-bonded network in the pores [1,2]. The $AlPO_4$-54•xH_2O structure at ambient pressure and temperature as derived from single crystal X-ray diffraction measurements, the occupancy of the disordered H_2O molecules in the pores was fixed to 50%, i.e. 36 H_2O molecules per unit cell (x = 2). Further 11 H_2O molecules were identified by MC simulations [4] and are too mobile to be localized by X-ray diffraction. The two types of water, i.e. from the aluminium octahedral and pore channels, were observed to interact, which is indicative of water ordering within the $AlPO_4$-54•xH_2O channels [10]. This model was later improved by assuming internal rotational motions of the bond water molecules about the Al-OH_2 bond and by allowing the relative populations of the bound and free sites to vary with temperature [2,11].

It was recently shown that water strongly modifies the mechanical response of $AlPO_4$-54•xH_2O structure [2,3]. While anhydrous $AlPO_4$-54 undergoes a phase transition to crystalline $AlPO_4$-8 around 0.8 GPa, with pore size reducing, $AlPO_4$-54•xH_2O becomes amorphous under pressure at about 2 GPa. It is noteworthy that the bulk modulus of the anhydrous $AlPO_4$-54 (B_0=12 GPa) is twice lower than its hydrated phase ($AlPO_4$-54•xH_2O, B_0=24 GPa). Combined X-ray diffraction and Monte Carlo molecular simulation studies have shown that when water act as pressure-transmitting medium (PTM) the onset of amorphization in $AlPO_4$-54•xH_2O decreases from 2 to 0.9 GPa [2,4] due to water insertion in the pore (x greater than 2). The PIA mechanism observed depends on the amount of water content in the porous. More specifically, when two water molecules enter in the coordination sphere of ^{IV}Al, thereby increasing the coordination number from 4 to 6, the structure destabilizes [2,4]. To provide additional information on the location of H_2O molecules in the zeolite structure, observed Fourier difference maps (F_{obs}) of electron density of $AlPO_4$-54•xH_2O under HP was calculated in Daphne 7474 (solution based on alkyl silanes and silicone oil) PTM and in water PTM from the structure refinements obtained by the synchrotron XRD single-crystal data [4]. This data treatments shows that water in the pore is highly disordered and the electron density broadening observed in the pore center with increasing pressure suggests that water is very mobile and exhibits a high-density liquid-like structure. However a direct investigation of water network through dynamical-vibrational studies is needed to corroborate this hypothesis and elucidate the water evolution during PIA.

Our objective is analyze the network of confined H_2O in $AlPO_4$-54•xH_2O nanocavities, by probing intra- and inter-molecular vibrations modes, going through its pressure-induced transition, and, thus to shed light on the role of water during PIA (0-2 GPa), together with low temperature measurements. Thereafter, yield information on changes in the bonding of water providing a microscopic description of thermochemical properties during the PIA. The proposed experiment plans to use INS to study the vibrational behavior of nanconfined water in $AlPO_4$-54•xH_2O zeolite pores as a function of both pressure and temperature. This first rapport will present the temperature results together with the perspectives in pressure. The INS spectrum clear shows the water libration dynamics bands, which cannot be probed by Raman and FTIR spectroscopy techniques, since this mode appear in the "shadow" of typical framework zeolite modes [2,3].

Experimental protocol. We performed inelastic neutron scattering (INS) measurements of the vibrational density of states (vDOS) of water confined at $AlPO_4$-54•xH_2O using IN1-Lagrange spectrometer (ILL, Grenoble) in a fixed-monitor regime with the 2D-focusing Cu220 monochromator. INS is an excellent technique to study energetics of water hydrogen bonding in confined media and it was already used in previous studies to provide information about translational modes onto hydrated minerals [5,6]. The vibrational spectrometer Lagrange is the unique spectrometer at the ILL that allows reaching the high energy transfer needed to study the inter- and intra-molecular vibrations. The scattering intensity from both the hydrated and dehydrated sample was collected at T = 10, 173, 235 and 293 K, using the Dysplex cryostat. 242 mg of $AlPO_4$-54•xH_2O was loaded into an aluminium sachet to give the sample thickness of ~2 mm for the low temperatures measurements. The data were collected over the range of 26-500 meV (172-4000 cm^{-1}). The more interesting results were obtained below 250 meV (2000 cm^{-1}). For each temperature measurements, typical data were collected between 26-150 meV with 0.5 energy step, between 151-300 meV with 1 meV energy step, and between 301-500 meV with 2 meV energy step. The spectra were accumulated over 6 h for each temperature in the aluminium sample holder and for about two cycles of 6 h inside the high pressure cell, which we plan to use for the HP characterization. In order to reach the GPa pressures needed to induce amorphization in the material, a high-pressure clump [7] available on Lagrange (reaching pressures up to about 2 GPa), will be used. Details could be find in the report experiment No. INTER-314.

Results. Since vibrations involving hydrogen dominate the incoherent inelastic neutron scattering spectrum, this technique is an ideal tool to probe the evolution of water nanoconfined in zeolite porous and others minerals, with a negligible contribution coming from the framework of the host material, considering no H in their structure. Meanwhile, $AlPO_4$-54•xH_2O has one-third of the aluminium cations octahedrally coordinate due to the presence of two H_2O molecules in their coordination sphere. In the case of the $AlPO_4$-54•xH_2O framework, considering the two H_2O molecules in the 6-fold coordinate Al, the total coherent and incoherent cross section turned out to be, $\Sigma_{coh} \approx 484.1$ barn and $\Sigma_{inch} \approx 1926.5$ barn. The cross section of the nanoconfined molecules per unit cell resulted in $\Sigma_{coh} \approx 271.1$ barn and $\Sigma_{inch} \approx 5618.2$ barn. Finally, the contribution to the total intensity coming from the zeolitic framework is about 29% and is mainly incoherent due to the two H_2O molecules from the octahedral Al. It must be considered that the Lagrange spectrometer has a limit detection of 1 mg of H in the sample content. In the two measured samples, 130 and 242 mg, the total amount of H mass content coming from the structural water (6-fold Al) are 0.62 and 1.15 mg, respectively. Though very low, this is not negligible and the contribution coming from the framework of the host material must be considered in future measurements.

The sample of $AlPO_4$-54•xH_2O was cooled to the cryostat base temperature at T = 10 K and subsequently warmed to 173, 235 and 293 K, Fig. 1 (left) show the INS spectrum of $AlPO_4$-54•xH_2O, from 172-4000 cm^{-1} at different temperatures. As will be commented later, at 293 K the zeolite has partially lost water, so this spectrum couldn't be taken in account for the final temperature study comparison. 3 main regions contribute to the INS spectrum and the bands are typical assigned to water specific vibrational modes. The region from 300 to 1200 cm^{-1} is typical of intermolecular librational modes (rotational oscillations). Around ~1625 cm^{-1} the HOH bending mode is visible. At highest energies, from 2500 to 4000 cm^{-1} the vibrational modes are due to OH stretching. The $AlPO_4$-54•xH_2O INS spectrum shows a strong band in the libration region (300-1200 cm^{-1}). Since the highest energy-part of the spectra (> 1250 cm^{-1}) did not present significant features, which could be likely better probed with others spectroscopy techniques (such as Raman or IR), we only studied and interpreted the region from 250 to 1250 cm^{-1} (31-156 meV). For a more straightful interpretation, our lower temperature spectra have been compared with the INS spectrum of ice Ih and ice low density amorphous (LDA) form, Fig. 1 (right).

Changes in the structure of the water are reflected in the intermolecular vibrational spectra, particularly the librational bands which are very sensitive to variation in hydrogen bonding [17]. In bulk water and ice there is a strong molecular coupling due to H-bonding forces, and the 3 librations of one uncoupled molecule will tend to give a broad band of frequencies. These will have a higher frequency in ice compared to water because of the more extensive hydrogen bonding. Considering that both types of water (from the aluminium octahedral and pore channels) in $AlPO_4$-54•xH_2O were observed to interact [10], the hydrogen-bond interaction from both between water/water of the pore and water-pore/water-framework is expected to become stronger decreasing the temperature. At the lowest temperature, T = 10 K, the INS spectrum of water confined in the $AlPO_4$-54•xH_2O shows some different features compared to bulk ice and LDA (Fig. 1–right): the librational band now has two better defined maxima, as in both ices, but not so well-defined maxima, and has broadened by shifting to lower frequency, together with less intensity than ices. The changes in the librational band suggest that the water in the zeolite channel, at T = 10 K, has a contribution from both, ordered and disordered (liquid like) structures, in which the number of H-bonds may be variable with a total average somewhat less than the four per molecule in hexagonal ice.

The spectral profile of the librational mode of $AlPO_4$-54•xH_2O can be very satisfactorily described by several overlapping Gaussian components after removal of a slowly rising linear background. This technique it was already successful applied to $AlPO_4$ molecular sieves into spectroscopy studies [3]. During the fitting procedure, the background was evaluated by as a straight line between two regions where no modes are observed. This linear background determined at the lowest temperature was then subtracted prior to the Gaussian fit and this background function was fixed and used for spectra at all temperatures. For clarity, we only present the librational band region prior to the background removal together with the fitted Gaussians and their assignment. Such a fit provides a sound tool to quantitatively account for the changes of librational modes, although the present Gaussian and background fit is not unique. The librational motions of water about the three principal axes of an isolated molecule are referred to as the wagging, twisting and rocking vibrations respectively, and only two of these are active in the IR and Raman. All three librations should be observed by neutron scattering. More specifically, these three subbands have been used considering to the three different librational modes of water molecules around its three symmetry axes: the x axis in the molecular plane, the y axis, which is the two-fold molecular symmetry axis, and the z axis perpendicular to the molecular plane (Fig. 1-right, insert). The observed subbands ω_1, ω_2 and ω_3, Fig. 1-right (insert), correspond to the librational modes around the axes y, z, and x, respectively [13-15]. The main fitting parameters, center frequencies and percentage intensities, as function of the temperature, are reported in Table I.

It is well-known that the position of the librational subbands can be roughly correlated with the strength of the hydrogen bonding, because strong hydrogen bonding produces a strong restoring force and, hence, a high frequency. From Table I, we can relate the high-frequency shift of the libration subbands passing from 235 and 173 to 10 K to a favoured formation of a more extended tetrahedral hydrogen-bonded network with stronger hydrogen bond. Which favoured the formation of more stable icelike arrangements at the pore surface. Supported by the analysis of the amplitude of the lowest Gaussians components, ω_1 and ω_2. This result is in agreement with previous single-crystal X-ray diffraction studies and MD simulations of $AlPO_4$-54•xH_2O at low temperatures, realised down to T = 173 K [1], which shows that water near the wall of the structure exhibit orientation order at lower temperatures.

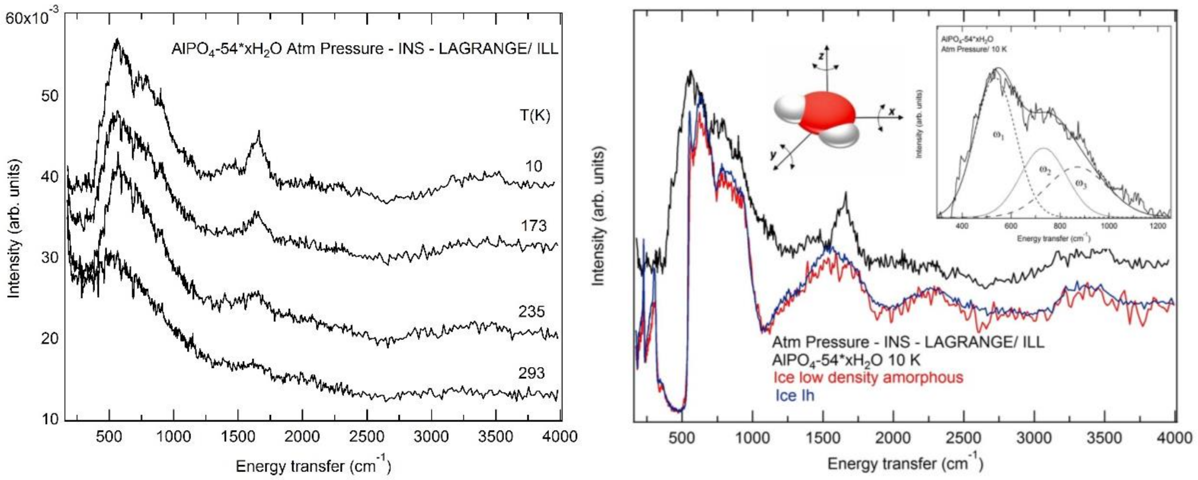

Figure 1. (*left*) INS spectrum of $AlPO_4$-54•xH_2O at T = 10, 173, 235 and 293 K. (*right*) INS spectrum of $AlPO_4$-54•xH_2O at 10 K (black line), ice Ih at T = 27 K (blue line)[8] and ice low density amorphous form (red line)[16]. Insert: Librational band for $AlPO_4$-54•xH_2O at T = 10 K together with the deconvoluted Gaussian components (dashed lines) corresponding to the three librational modes around the three symmetry axes of water molecules (see insert; H white sphere, O red sphere).

Finally, the $AlPO_4$-54•xH_2O INS spectrum were measured at ambient and low temperature, 293 and 173 K respectively, and atmospheric pressures inside the high pressure cell with objective to evaluate the quality of the libration band of the $AlPO_4$-54•xH_2O nanoconfined water, Fig. 2. As could be observed, the INS spectrum of the libration band inside the high pressure cell shows 5 times less intensity and high background noise/signal, due to the strong absorption of the cell together with the half mass of sample. Nevertheless, the libration band showed the same shape form in both acquisitions. Comparing both spectra at ambient temperature (Fig. 2-right), we conclude that the sample contained in the aluminium sachet had lost most of hydration water at the end of the temperature study. The high pressure cell sailing (Fig. 2-left) avoided the water lost during vacuum pumping at that temperature.

Table I. Center frequencies and percentage intensities of the $AlPO_4$-54•xH_2O librations bands.

T (K)	ω_1 (cm^{-1})	I_1 (%)	ω_2 (cm^{-1})	I_2 (%)	ω_3 (cm^{-1})	I_3 (%)
10	549.2	46.1	767.3	36.6	947.2	17.3
173	547.2	45.1	761.1	35.9	946.5	19.0
235	545.2	43.4	711.8	35.8	896.8	22.8

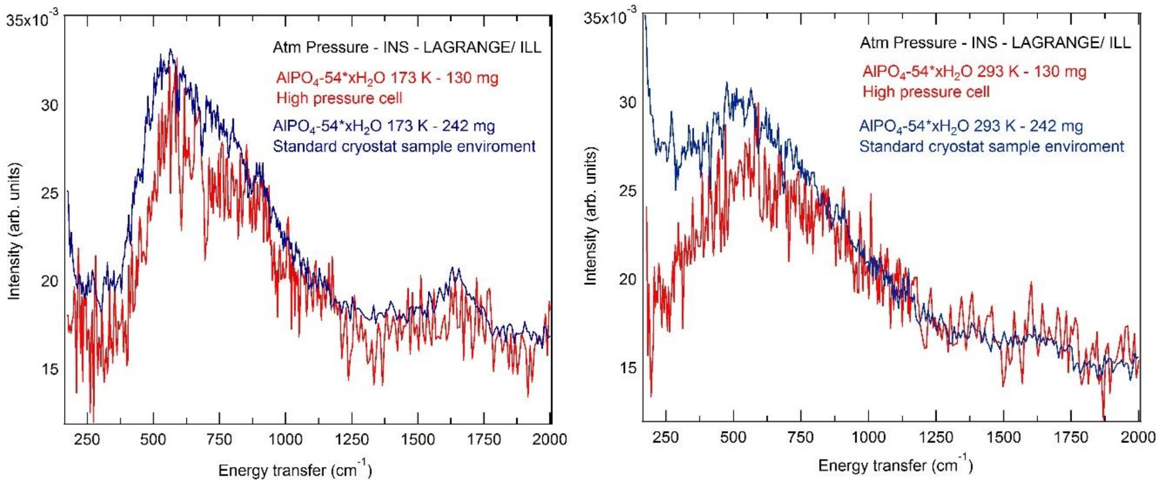

Figure 2. INS spectrum of $AlPO_4$-54•xH_2O at the cryostat sample holder (blue curve) and inside the high pressure cell (red curve) at T = 173 K (*left*) and at T = 293 K (*right*). For the sake of clarity, the intensity of the spectrum inside the high pressure cell (red curve) has been multiplied by 5.

References.

[1] Alabarse, F. G. et al. Phys. Rev. Lett. 109, 035701 (2012).
[2] Alabarse, F. G. et al. J. Phys. Chem. C, 118, 3651 (2014).
[3] Alabarse, F. G. et al. J. J. Phys. Chem. C, 119, 7771-7779 (2015).
[4] Alabarse, F. G. et al. J. Am. Chem. Soc. 137, 584−587 (2015).
[5] Ockwig N. W. et al. J. Am. Chem. Soc. 131, 8155–8162 (2009).
[6] Ockwig N. W. et al. J. Phys. Chem. C, 112, 13629–13634 (2008).
[7] Klotz, S. Techn. in High Press. Neutron Scatter. CRC Press, 2013 – New York.
[8] Li, J. J. Chem. Phys. 105, 6733 (1996).
[9] Ivanov, A. et al. J. Journal of Physics: Conference Series 554, 012001 (2014).
[10] Goldfarb, D. et al. J. Am. Chem. Soc. 114, 3690−3697 (1992).
[11] Duer, J. M. et al. J. Phys. Chem. 98, 1198−1204 (1994).
[12] Alabarse, F. G. et al. J. J. Phys. Chem. C, 119, 7771-7779 (2015).
[13] Rahman, A. et al. J. Chem. Phys. 55, 3336 (1971).
[14] Hall, P. G. et al. J. J. Colloid Interface Sci. 79, 339 (1981).
[15] Crupi, V. et al. J. Phys. Chem. B106, 10884 (2002).
[16] Li, J.C. J. Chem. Phys. 105, 6733-6755 (1996).
[17] Ramasay, J.D.F. et al. Journal de Physique Colloques. 45 (C7), C7-73-C7-79 (1984).