Hydrogenous materials using powder neutron diffraction: full structural determination of adsorbed water molecules in a zeolite†

Paul F. Henry,*[a] Mark T. Weller[b] and Chick C. Wilson[c]

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A full structural description, including the adsorbed water molecules, of the zeolite goosecreekite $CaAl_2Si_6O_{16}\cdot 5H_2O$, has been obtained from powder neutron diffraction data in one hour, illustrating the potential of modern instrumentation for characterization of hydrogenous materials without deuteration.

Zeolites continue to be widely used in the chemical industry with applications including molecular adsorption (*e.g.* separation and drying), ion exchange (*e.g.* environmental pollution control and water softening) and catalysis.[1,2] The positions and distributions of molecular species contained within the zeolite pores and their interactions with the framework and any charge balancing cations are of great importance in determining the performance of zeolites for catalysis and ion exchange. Therefore, a full understanding of their structures is crucial in the optimization of materials for applications. However, in ion exchange applications, the role of water is often poorly understood due to lack of hydrogen positions in the published structures. Similarly, for catalysis and molecular adsorption, the interaction of solvent molecules or adsorbed organic species with both the framework and extra-framework cations is generally poorly understood by diffraction techniques. Modern computational methods provide a route to calculating the most stable geometries for the framework, charge balancing counter cations and the water molecules[3] but there is need for accurate complete experimental structural information to validate and develop the theories.

Hydrogen (H) positions in inorganic materials have been traditionally determined using neutron diffraction data as the contribution of hydrogen to the full X-ray diffraction pattern is usually very small. Deuterated samples have been used as the large incoherent scattering contribution from hydrogen typically yielded statistically very poor data, due to low count-rate instruments and available neutron fluxes. However, for a large number of systems with technological interest, such as natural zeolites, clathrates and many supramolecular systems, deuteration is impossible or proceeds incompletely, is too expensive and overly time-consuming. For example, calcium-based zeolites are very difficult to synthesize[4] and, even where routes have been found, reactions generally take months rather than days. Complete deuterium (D) exchange in such systems, necessary due to the opposite and contrasting neutron scattering lengths of H and D, is also impossible practically due to the strong divalent cation to water molecule interaction. Strong H–D isotope effects are also seen with many zeolite applications, including ion exchange and catalysis, making characterization of the hydrogenous-form crucial in terms of understanding the true properties.[5,6]

Recently, we have shown that modern powder neutron instrumentation has a significant role to play‡ in the rapid structural characterization of hydrogenous materials[7] and we demonstrate herein the application of the technique to zeolite systems. The natural zeolite goosecreekite was chosen for a case-study as the hydrogen positions were unknown and it provides the opportunity to validate the computational modeling of this zeolite structure.[8–10] Goosecreekite ($CaAl_2Si_6O_{16}\cdot 5H_2O$, IZA code GOO) is a rare natural zeolite mineral that occurs as block-like or irregular crystal growths on matrices such as quartz, amethyst and stilbite and is one of a number of natural minerals that have not been synthesized. A sample of goosecreekite from Jalgaon, Maharashtra, India was obtained in the form of multiply twinned crystal growths on a quartz matrix. Material was chipped from the surface of the matrix and thoroughly ground to give a homogenous powdered sample. Due to the nature of the growths, it was not possible to find a crystal suitable for single-crystal neutron diffraction. Powder X-ray diffraction (PXD) data were collected over the 2θ range 10–60° with a step size of 0.02° using a Siemens D5000 diffractometer (Cu-Kα_1 radiation, λ = 1.54056 Å) operating in Bragg–Brentano geometry for phase quantification. Powder neutron diffraction data were collected on a 2 g sample in a standard 7 mm cylindrical vanadium sample holder for 1 h using the D20 instrument[11] at ILL, France in its high takeoff angle setting[12] using a neutron wavelength of 1.87 Å, Ge(115), under ambient conditions. Rietveld refinement was performed using the GSAS suite of programs[13] and the EXPGUI interface.[14]

The best, though incomplete, structure determination of goosecreekite was published in 1986 using single-crystal X-ray diffraction data by Rouse and Peacor[15] but the data were not of sufficient quality to locate the hydrogen positions.

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[a] *Institut Laue-Langevin, 6 Rue Jules Horowitz, BP156, 38042 Grenoble Cedex 9, France. E-mail: henry@ill.fr; Fax: +33 (0)4 7620 7648; Tel: +33 (0)4 7620 7604*
[b] *Chemistry School, University of Southampton, Highfield, Southampton, UK SO17 1BJ. E-mail: mtw@soton.ac.uk; Tel: +44 (0)23 8059 3592*
[c] *Department of Chemistry and WestCHEM Research School, University of Glasgow, Joseph Black Building, Glasgow, UK G12 8QQ. E-mail: c.c.wilson@chem.gla.ac.uk; Tel: +44 (0)141 330 8522*

† Electronic supplementary information (ESI) available: Full structural information (CIF file, atomic positions, Rietveld fits and bond distances/angles) for the O–H unconstrained and constrained models and the TGA/DTA plot of the dehydration of goosecreekite. See DOI: 10.1039/b719464a

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Goosecreekite crystallizes in the monoclinic space group $P2_1$ with the lattice constants a = 7.401(3) Å, b = 17.439(6) Å, c = 7.293(3) Å and β = 105.44(4)° (after Rouse) and the framework consists of a three-dimensional channel structure of 8-, 6- and 4-rings of tetrahedrally coordinated aluminium and silicon atoms (T atoms) with calcium as the charge balancing cation in the pores, which is coordinated to five water molecules and directly to the framework. The channel pores have a maximum opening of 4.7 × 2.9 Å. Deuteration of natural goosecreekite, by ion exchange in deuterated water under elevated temperature conditions or by complete dehydration followed by rehydration under a deuterated water atmosphere, was unsuccessful. In the former case the deuteration was incomplete, even after repeated cycling, and in the latter case an irreversible collapse of the framework to a highly stable orthorhombic structure results.[16] Both of these results illustrate the tight binding of the water molecules by the framework and the calcium counter cation and its role in stabilizing the structure.

The PXD pattern was matched with that expected for goosecreekite[17] with a small amount of residual quartz from the host matrix (<5%). The initial model for the Rietveld refinement was that of Rouse and Peacor.[15] In order to obtain initial hydrogen positions, rigid body water molecules were modelled with the oxygen positions defined from the previous work. The five water molecules were then allowed to translate and rotate freely with the framework kept fixed in order to find the correct approximate orientations. The rigid body constraints were then removed so that the water molecule positions could be varied and refined. Due to the large number of atomic positions (40 atoms on general positions), tight soft constraints were applied to the framework and the water molecule bond lengths (bond lengths Si–O = 1.625 Å, Al–O = 1.725 Å and O–H = 1.00 Å with esd of 0.001 Å) and isotropic atomic displacement parameters were set to be identical for the same atom types in order to reduce parameter correlation (<120 independent variables in the isotropic atomic displacement parameter case). No constraints on the T–O–T framework and water molecule bond angles were used. All data on this soft constraint model have been deposited as ESI.† Further analysis, which released the bond-length soft constraints, led to very similar fit parameters to the data, with higher esds due to the increased parameter correlations and results are also included in the ESI.†

Fig. 1 shows the fitted profile to the data and the high Q-region is expanded in the ESI.† The incoherent scattering contribution is clearly seen but the data show that the signal : noise ratios are very good, even at high Q. In the case of each of the water molecules the isotropic atomic displacement parameters of the three atoms (2 H and 1 O) were constrained to be equivalent and the occupancy fixed at 1.0 as thermogravimetric measurements had confirmed full water content. Fig. 2 shows the final refined structure, highlighting the coordination geometries of the calcium within the pores and Tables 1 and 2 give the relevant counter-cation and water bond-distances and angles, respectively. Of particular note is the anomalous behaviour of the water molecule W2. The refined bond angle of 89.2(17)° is much less than the other water molecules, which are well within expected values from a refinement of this type and lie close to the ideal value of 108.7°. From the refinement and Fig. 2, W2 is the only water molecule that does not have at least one strong H-bond to the framework and is also the only water molecule with a weak intermolecular water H-bond distance, 2.264(24) Å. The poorer definition of this water molecule is a result of it undergoing significant motion at room temperature due to its weak binding into the structure. As stated previously, the proposed models from the recently published computational work[9,10] do not list atomic positions and so no direct comparison of the experimentally determined full structure to that from computational analysis can be presented here.

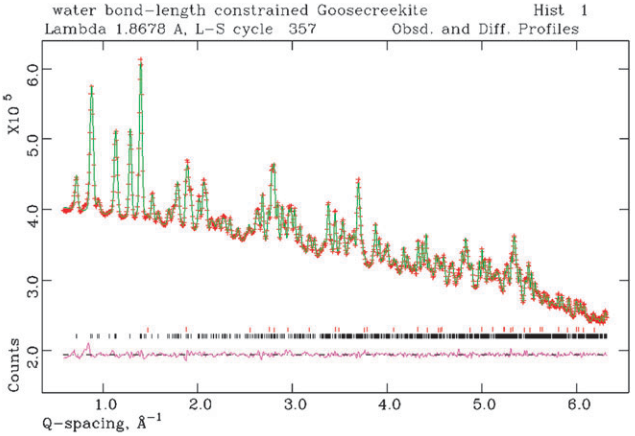

Fig. 1 Final Rietveld refinement profile for goosecreekite for the bond length constrained model. The observed data are crosses, the calculated pattern a solid line, the tick marks show the allowed reflections (upper quartz, lower goosecreekite) and the lower solid line is the difference plot; R_{wp} = 6.6%, R_{p} = 5.0% and $R_{\mathrm{F**2}}$ = 3.01% for 1089 observations.

There has also been significant interest in the role of water in determining the structure of goosecreekite during hydration/dehydration by computational methods[9,10] and also in the relationship of goosecreekite to other similar calcium aluminosilicate minerals Yugawaralite and Wairakite.[18] Various mechanisms have been proposed from the computational studies but only an *in situ* neutron diffraction experiment can probe directly the mechanisms involved for validation purposes. The thermogravimetric analysis (TGA) and

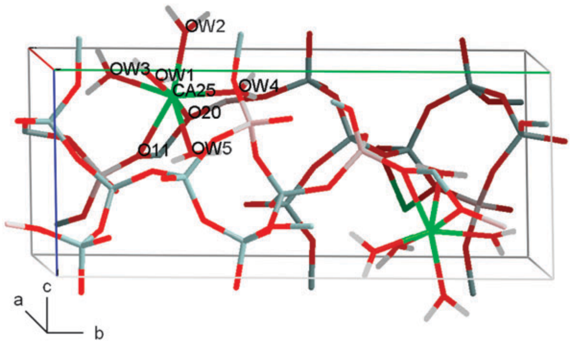

Fig. 2 The structure of goosecreekite from the bond-length constrained model observed close to the *bc*-plane. The coordination sphere of the calcium is highlighted by labelling.

Table 1 Relevant bond distances (Å) and angles (°) in goosecreekite illustrating the calcium coordination sphere and the H-bonding to the framework

Bond	Distance/Å	Bond	Distance/Å
Ca–O11	2.536(15)	O17–H2W1	1.906(14)
Ca–O20	2.399(15)	O15–H1W2	2.212(18)
Ca–OW1	2.396(19)	O10–H2W2	2.207(19)
Ca–OW2	2.309(16)	H2W2–OW5	2.264(24)
Ca–OW3	2.371(17)	O12–H1W3	1.841(13)
Ca–OW4	2.347(19)	O9–H2W3	1.875(16)
Ca–OW5	2.497(18)	O21–H1W4	1.728(17)
Av. Si–O[a]	1.625(4)	O13–H2W4	2.121(14)
Av. Al–O[a]	1.725(3)	O14–H1W5	1.814(16)
Av. O–H[a]	1.00(1)	O16–H2W5	2.038(14)
O23–H1W1	2.144(18)	O10–H2W5	2.277(21)

[a] Constrained bond lengths.

Table 2 Relevant bond angles in the water molecules in goosecreekite

Bond	Angle/°	Bond	Angle/°
H1W1–OW1–H2W1	110.1(18)	H1W4–OW4–H2W4	112.7(18)
H1W2–OW2–H2W2	89.2(17)	H1W5–OW5–H2W5	111.0(18)
H1W3–OW3–H2W3	105.1(14)		

differential thermal analysis (DTA), deposited in the ESI,† show that there is a partially dehydrated structure stable between 100 and 250 °C, which nominally has four zeolitic water molecules from the weight loss, followed by a two other weight-loss events in the region 280–300 and 350–400 °C, associated with significant endothermic reaction peaks in the DTA. Nothing is known experimentally about the structure of the intermediate phase and the water loss events leading to the structural collapse. A short experiment following the dehydration process *in situ* was performed on D20 and illustrated that high quality structural data should be obtainable as a function of temperature through each of the weight-loss events. Further *in situ* data collections under optimized conditions will investigate the reversibility of the first water loss and the relationship of the further water loss events to the high-temperature structural phase change.[19]

In conclusion, despite the incoherent scattering from hydrogen that is clearly seen in the experimental data, the structural refinement is robust, chemically sensible and is a significant step forward on all the previous experimental structural studies. The work clearly shows that with the correct instrumentation the long held beliefs that hydrogenous materials and powder neutron diffraction are incompatible and that deuteration is an absolute requirement are no longer valid. In addition, the short timescale required to obtain high quality statistics, in this case 1 h, on a material that contains 25 atom% H is striking and illustrates the potential of powder neutron diffraction to become a standard tool in the armoury of the materials scientist for hydrogenous materials and opens up the possibility to investigate technologically important hydrogenous system properties directly *in situ*, such as hydrogen storage material uptake/release kinetics, fuel-cell processes, ion-exchange/mobility and clathrate formation/stability. Studies of the type described here on hydrogenous minerals will also allow improved computational modeling of these and similar systems.

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Notes and references

‡ In the specific case of D20 at ILL, the combination of a very high incident neutron flux coupled with a high monochromator takeoff angle and large area-detector yield high counting rates with good resolution over an extended *d*-spacing range ($\Delta d/d$ minimum $\sim 2 \times 10^{-3}$) that allows data collection for full structural refinement in seconds to minutes for moderately complex powder samples. When applied to hydrogenous materials this becomes of the order of minutes to hours to give saturated counting statistics, depending on the sample volume, unit cell size and space group, number of atoms in the asymmetric unit and hydrogen content.

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