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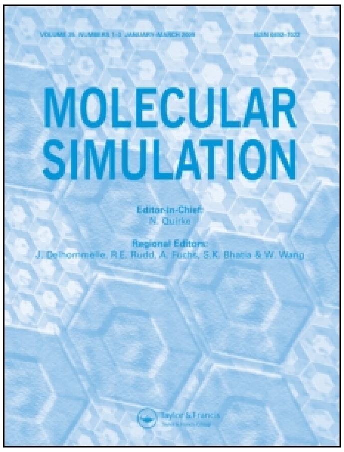

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Modelling of hydrated Ca-rich zeolites

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Online publication date: 26 October 2010

To cite this Article Lewis, Dewi W. , Ruiz-Salvador, A. Rabdel , Almora-Barrios, Neyvis , Gómez, Ariel and Mistry, Manisha(2002) 'Modelling of hydrated Ca-rich zeolites', Molecular Simulation, 28: 6, 649 — 661

To link to this Article: DOI: 10.1080/08927020210871

URL: http://dx.doi.org/10.1080/08927020210871

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Molecular Simulation, 2002 VOL. 28 (6-7), pp. 649–661

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MODELLING OF HYDRATED CA-RICH ZEOLITES

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(Received 1 April 2001; In final form 1 August 2001)

The successful modelling of the structure of two hydrated calcium-rich natural zeolites is described, showing how modelling can reproduce their complex structure, in excellent agreement with experiment. Furthermore, we demonstrate how such methods are able to determine the preferred Al ordering in the mineral Goosecreekite. The dehydration behaviour of Goosecreekite is also predicted. The interatomic potentials for water, evaluated here, are found to be robust and transferable to zeolitic materials.

Keywords: Natural zeolites; Goosecreekite; Gismondine; Modelling; Hydration

INTRODUCTION

Over the past 20 years, computational methods have been extensively applied to study zeolites and other microporous solids. A prime motivation has been wide application of zeolites in the field of catalysis: witness the many studies of the sorption and transport of reactants and products and also the reactivity of the acid centres within these materials [1]. However, the largest tonnage use of zeolites is

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ISSN 0892-7022 © 2002 Taylor & Francis Ltd
DOI: 10.1080/08927020290030189

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for ion exchange, primarily for water softening in domestic detergents but also in heavy metal and radioisotope cleanup. These applications, in contrast to those in catalysis, rely on the use of hydrated zeolites; the intrazeolitic water being the transport medium for the exchanging ions. Similarly, all natural (and many synthetic) zeolites exist under normal conditions in the hydrated state. Indeed, many are unstable to dehydration. In common with many other areas of chemistry and materials science, the theoretical/computational study of such hydrated materials has hitherto being considered either too complex—water being difficult to model—or too expensive to perform. Recently, there have been some attempts to study hydrated zeolites [2–6] but some of these have either been on systems where hydration has little impact on the overall structure of the material [2,3] or have been shown to be difficult and unable to reproduce experiment [4]. In particular, Hill *et al*. [4] were unable to find a suitable potential set for a model of hydrated zeolite Na-MAP that could be used to interpret their diffraction results.

Our work in the area is stimulated by our studies [7–9] of the structure of the polymorphic minerals clinoptilolite and heulandite. Both are abundant minerals and have properties which can be exploited in both traditional areas of ion exchange [10] but also as carriers for pharmaceutical agents [11]. In our previous work we have modelled dehydrated materials with some success. For example, we have been able to successfully reproduce the experimental distribution of Al over the various T sites in these materials as well as identifying many extra-framework sites for both monovalent and divalent cations. However, a number of the cations sites were seen to be displaced from their experimental sites towards the framework, in order to maximise their coordination with the framework oxygen. Clearly, these discrepancies can be ascribed to our omission of water from our models. Therefore, in order to move this work forward, we have attempted to include hydration via the potentials of de Leeuw *et al*. [12,13] and have evaluated their use in zeolites. We present first our reproduction of the experimental structure of the hydrated material Gismondine, and also our study of the role of water in controlling the ordering of Al in the framework of Goosecreekite. We also discuss the implementation of the model and issues arising from its use in zeolitic systems.

METHODOLOGY

Calculations were performed using GULP (General Utility Lattice Program) [14]. Short-range interactions are calculated in real space within a 16 Å cut-off and the electrostatics treated by an Ewald summation. Energy minimisations were initially performed using a Newton–Raphson method, updating the Hessian

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matrix by the BFGS approximation. After a suitable convergence of the gradients, the RFO minimiser was then used. The latter, despite being considerably more expensive, is highly recommended as it drives the system to a true minimum, with no imaginary modes and avoids other stationary states. A convergence criterion of 0.001 eV/Å was used.

The complex potential energy surface of these systems precluded a simple, one-step, constant pressure minimisation, and a step-wise minimisation procedure was used. For example, allowing first only the water to optimise under constant volume, then constant pressure; shell optimisation of the framework followed by constant volume minimisation of the framework; re-optimisation of the water at constant volume; followed by a final constant pressure optimisation of the entire structure. Whilst time-consuming, no other method allowed the optimiser to successfully converge to minimised structures.

A formal charge Born model is used with interatomic potentials. For modelling the interactions within the framework and between the framework and the extra-framework calcium cations, we employed the potentials described by Jackson and Catlow [15]. These potentials include polarisation via a shell model for the framework oxygen and are augmented with a three-body term to account for the partial covalency of the zeolite framework. The potential parameters for water are those derived by de Leeuw *et al*. [12,13], which were obtained for the modelling of solvation at ionic mineral surfaces. They are, therefore, more suitable for simulations of hydrated zeolites (where the most accurate models are also formally charged) than other water potentials such as those derived for modelling proteins and other biomolecules. They also include a description of polarisation (the water oxygen core and shell charges being -2.05 and 1.25, respectively) that will be significant in stabilising low symmetry configurations. The interactions between the water and the oxygen of the zeolite framework were initially taken from the work of de Leeuw *et al*. [12,13] but were subsequently modified (see below).

RESULTS AND DISCUSSION

Gismondine

As a first test case we considered the mineral Gismondine (IZC structure type code GIS) in its calcium form, which was chosen for a number of reasons. First, it has an Si/Al=1 and therefore an unambiguous framework structure. Secondly, it has been well characterised by XRD [16,17] with various water contents: furthermore, the water is well localised and strongly coordinated to the extra-framework calcium cations. Thirdly, zeolite MAP, which is used in detergency applications, is isostructural with Gismondine. Previous computational studies [4] have not found interatomic potential methods fruitful for identifying water positions in Na-MAP with the authors resorting to expensive DFT calculations. The unit cell is ideally $Ca_4Al_8Si_8O_{32}.18H_2O$ with an orthorhombic unit cell of approximately $10 \times 10 \times 10\,\text{Å}$ [16]. The framework can be described as consisting of two double crankshaft chains, one parallel to [100] and another parallel to [010]. The pores interconnect forming a three-dimensional channel system with 8-ring openings of diameter $\sim 3.0 \times 4.5\,\text{Å}$. At the channel intersection, a cavity is formed containing Ca cations surrounded by three fully occupied and two partially occupied water molecules. The Ca^{2+} also coordinate to framework oxygen atoms.

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We constructed a model for an almost fully hydrated Gismondine with 16 H_2O molecules per unit cell from the crystallographic study of Vezzalini *et al*. [16]. Only oxygen positions were reported for the water molecules and hydrogen positions were generated in MSI's Cerius^2 software [18]. The water molecules were orientated manually to maximise coordination to the Ca^{2+}. For the few water molecules that do not coordinate directly to calcium, judgement was used to manually orientate the molecules to maximise interactions with the framework. We also constructed a model of the partially dehydrated structure, with 8 H_2O per unit cell from the same study, which has a larger unit cell due to a lowering of the symmetry.

Energy minimisation of these structures was performed using the step-wise procedure outlined above. We found the potential energy surface to be very complex which resulted in the calculations being very difficult to bring to convergence. The small contribution of the energy of the water molecule and, in particular, its interaction with the framework, to the total energy, means that the minimisation algorithms have great difficulty in following the correct energy gradients. Thus, the tolerances and accuracy used by the algorithms had to be significantly increased to ensure convergence. Similarly, the maximum displacement of atoms during a minimisation step was reduced to ensure that the minimiser was not simply hopping back and forth between local minima. During this work we found that the short-range terms between the water and the framework were not repulsive enough at very short distances—the co-called "Buckingham catastrophe". This often resulted in the water molecule being dragged into the framework—when the T-Ow distance was typically 1.8 Å—by the very strong Coulomb interaction between the framework Si and Al and the oxygen of the water. Modifications were thus made (see below) to the T-Ow potential to make it more repulsive at these short distances, although care was taken to ensure that the energy surface at more reasonable distances remained

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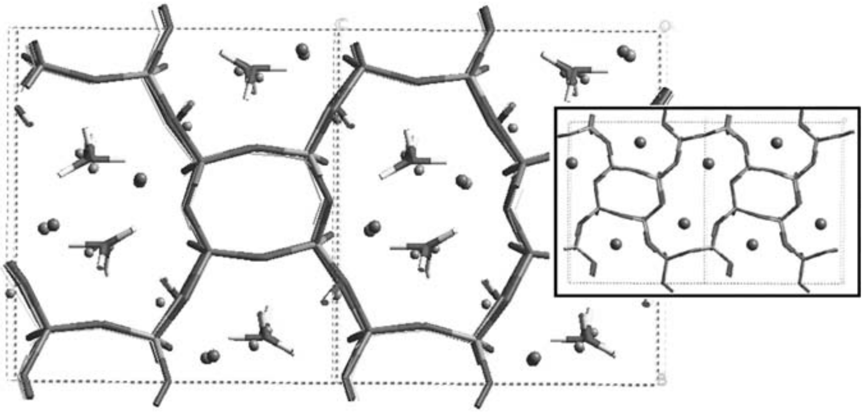

FIG. 1 Gismondine with 16 water molecules per unit cell. The experimental structure [16] is shown in grey. Inset is the same unit cell when energy minimised without water. Note the severe distortion of the channels and the rotation of the four-membered rings.

unchanged. This highlights the difficulties in using this (or any) water potential within the very strong electric fields of zeolite pores, which are significantly different from those of the mineral surfaces, for which they were derived [12,13].

The final calculated structures of the fully and partially dehydrated Gismondine materials are given in Figs. 1 and 2 and unit cell parameters and cation–oxygen distances are reported in Table I. Overall, the agreement is excellent with a maximum deviation in unit cell parameter of 3.8% and 0.8% for the 16 and 8 water molecule structures, respectively. The agreement is

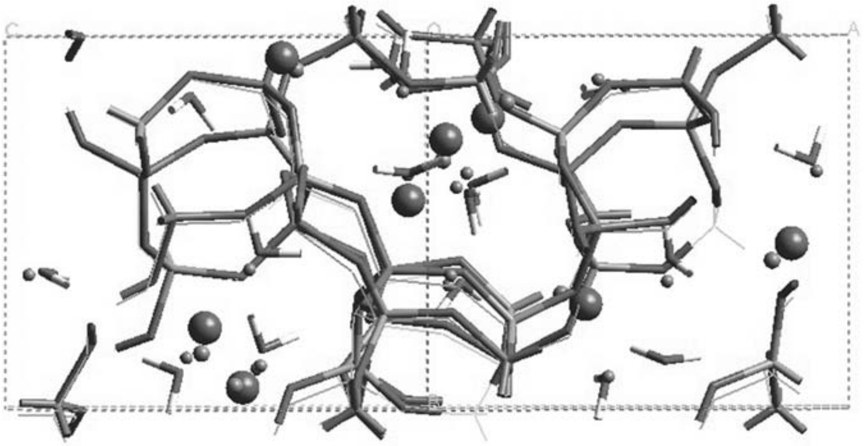

FIG. 2 Gismondine with 8 water molecules per unit cell. The experimental structure [16] is shown in grey.

TABLE I Unit cell dimensions for Gismondine with 16 and 8 water molecules per unit cell. Also shown are the calculated values for a wholly dehydrated unit cell. Note that the unit cell used for the calculation with 8 water molecules is different to that used for 16 water molecules [16], the cell being larger by a factor of $\sqrt{2}$ in a and c. The dramatic changes in cell volume on reducing the water content is clear (~ 17% for both calculation and experiment) and further emphasised by the large volume change in the unit cell with no water

	a (Å)	b (Å)	c (Å)
16 H_2O			
Experimental	9.989	10.616	9.820
Calculated	9.611(− 3.8%)	10.654(− 0.4%)	9.684(− 1.4%)
Dehydrated			
Calculated*	8.701(− 13%)	10.584(− 0.3%)	8.142(− 17%)
8 H_2O			
Experimental	13.790	8.594	13.889
Calculated	13.791(< 0.1%)	8.666(+ 0.8%)	13.923(+ 0.3%)

* The dehydrated cell is calculated from the 16 H_2O unit cell [16] without water and errors are relative to the 16 H_2O cell.

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particularly good if compared to those results obtained for a dehydrated unit cell (Fig. 1 inset). When the structure is minimised without water being included, there is significant pore collapse and the cations are displaced to maximise their coordinated with the framework. Average Ca-framework oxygen and Ca-water oxygen distances in the 16 H_2O unit cell are 3.21 and 2.52 Å, respectively—the same as in experiment. The water molecules that are not strongly coordinated are orientated so as to form some weak interactions with the framework. The partially dehydrated structure is also in good agreement with that obtained by experiment. The hydrogen positions in the two minimised structures are all consistent, giving an average OH distance and H–O–H angle of 0.98 Å and 102.2°, respectively. From these simulations, it is clear that the potential parameters are robust and able to reproduce hydrated zeolite structure.

Goosecreekite

The aim of our study of Goosecreekite was to determine the influence of water on the positioning and ordering of Al within the framework. Our previous work in medium Si/Al zeolites [7–9] such as clinoptilolite and heulandite had been successful in reproducing experimental populations determined by crystallography: our methodology for investigating Al distributions is described therein. We wished to further test our method and also to determine if water had a significant role in determining Al distributions.

Goosecreekite was chosen for the following reasons. Firstly, it has a Si/Al=3 which is found to be ordered experimentally [19]. Furthermore, it has a low

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symmetry (spacegroup $P2_1$) with eight unique tetrahedral sites each with a multiplicity of 2: six of the sites are found to be occupied by Si (labelled Si1, Si2,. . .,Si6), the remaining two sites by Al (Al1 and Al2) [19]. Thus, the material would present a difficult test of our sampling method for locating the most stable structures. It also has a small pore volume, in which the water molecules are all strongly coordinated to the extra-framework Ca^{2+}, allowing us to investigate more closely the interaction of the water with the extra-framework cations.

Our study of the ordering of Al in the framework proved to be highly successful—further details are given in Ref. [20]. In summary, we found that our sampling method was able to determine that ordered Al distributions were the most stable; two ordered configurations have a calculated Boltzmann population of 53% and 23% of the total sample at typical synthesis conditions. However, we find that the most stable configuration does not have the Al at the correct positions: the second most stable does. Again, these initial calculations were performed without including water.

On repeating the calculations for these two most stable configurations with the inclusion of water, we find that the structure with the same Al ordering (and cation location) as experiment is now the most stable. Fig. 3 shows our final calculated (hydrated) structure compared to that determined experimentally. Agreement with the experimental structure is excellent (see Table II) with the maximum error being 2.4% in the **b** parameter. The geometry of the extra-framework species is also in excellent agreement, with the Ca^{2+} being coordinated to five water molecules and two of the framework oxygen atoms. The

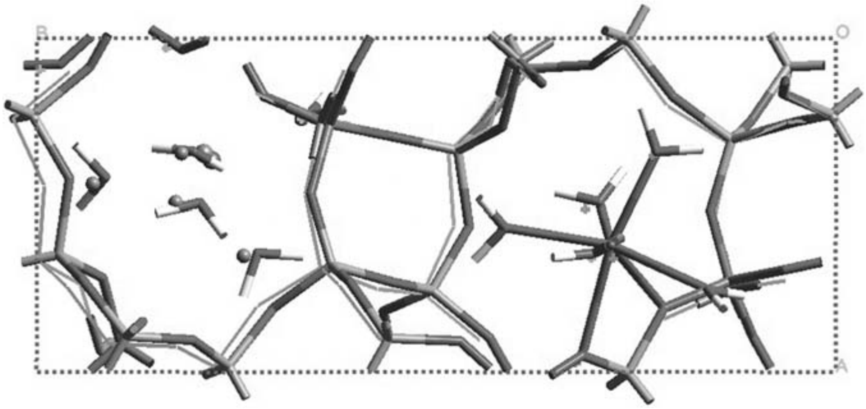

FIG. 3 The most stable calculated structure of Goosecreekite with water and the experimental [19] unit cell (grey lines with Al highlighted as tubes). Highlighted in the right channel is the coordination sphere of the Ca^{2+}. Also shown are the experimental water oxygen and Ca^{2+} (grey crosses and spheres) positions for comparison to the calculated sites (tubular water and larger spheres).

TABLE II The unit cell parameters for the ordered Goosecreekite unit cell, with and without water are given and compared to experiment. When water is included, this configuration (the same framework distribution as experiment) is the most stable configuration found. However, when water is omitted it is the second most stable, with another order Al distribution (not that found by experiment) being more stable (see Ref. [20] for further details). For each structure the cell angle α and γ are calculated to be 90.00°. Experimentally $\alpha=\gamma=90°$

	a (Å)	b (Å)	c (Å)	β (°)	Volume (Å^3)
Expt [19]	7.401	17.439	7.293	105.4	907.3
No water	7.409(+0.2%)	17.036(−2.3%)	7.155(−1.9%)	109.1(+3.5%)	789.1(−13.0%)
With water	7.398(−0.1%)	17.017(+2.4%)	7.236(−0.8%)	106.3(+0.9%)	874.0(−3.7%)

maximum error in Ca-O distance is $<5\%$, which is in line with the overall error in the unit cell dimension: Table III provides some of the key distances.

Dehydration of Goosecreekite

In addition to the fully hydrated and dehydrated structures discussed above, we have also attempted to predict the structural changes that Goosecreekite would undergo on dehydration. To do so, we took the calculated fully hydrated structure and removed each water molecule in turn (leaving nine H_2O molecules) and re-optimising. The most stable structure (with nine H_2O molecules) was then selected and the removal of a water molecule repeated. The process was repeated until no water remained. The final structure obtained was the same as that found from our initial consideration of the anhydrous structure.

From these calculations, we are able to construct a dehydration profile of the material (Fig. 4). As expected, the removal of water leads to a less stable structure. More significantly, large changes in cell parameters occur (see Fig. 5). We also note that the dehydration procedure results in a "symmetrical" dehydration of the two cations in the unit cell; each loses a water molecule in-turn

TABLE III Ca–O distances in hydrated Goosecreekite. Figures in italics are to framework oxygen, the remainder to water

Calculated (Å)	Experimental (Å)	Error (%)
2.48	*2.42*	*2.7*
2.67	*2.54*	*4.9*
2.23	2.34	−4.4
2.29	2.37	−3.2
2.32	2.42	−4.3
2.34	2.45	−4.4
2.34	2.45	−4.3

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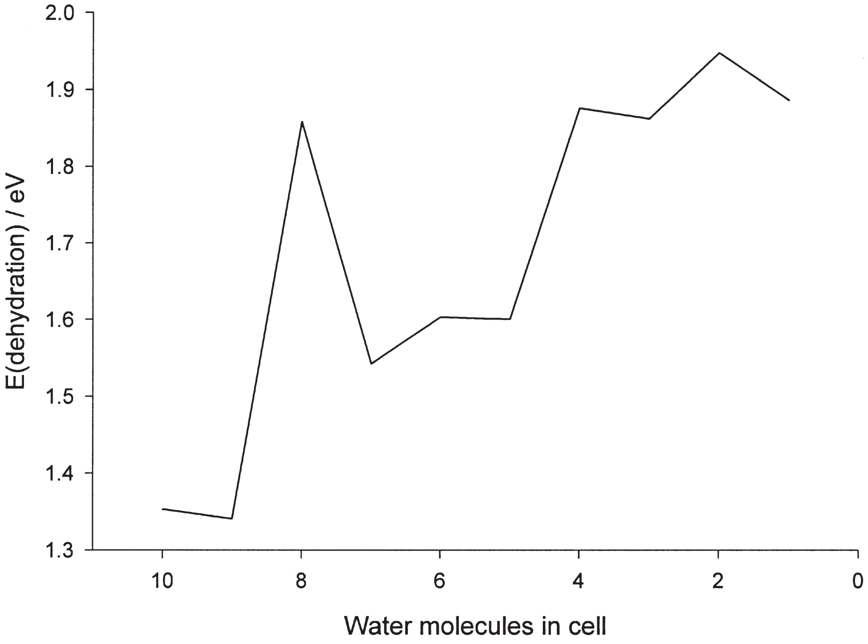

FIG. 4 Calculated dehydration profile of Goosecreekite. The energy released on the removal of each water molecule to the gas phase is plotted. The numbering of water molecules refers to the removal of the *n*-th water molecule.

rather than one becoming more dehydrated than the other. Indeed when the unit cell has an asymmetric distribution of water molecules (an odd number) the energy required to remove the next water molecules is lower. For example, removal of the 2nd water molecule is actually easier than removing the 1st, similarly, the 4th is much more readily removed than the 3rd. As the material dehydrates, the unit cell contracts, the pore dimensions also gradually contract and the cations migrate from their central position in order to satisfy their coordination via the framework oxygens. Note how there is rapid shrinkage in **a** and **b** below four water molecules whilst **c** actually expands again. The latter expansion is due to the pores becoming elliptical as the Ca^{2+} coordinate across the pore diameter.

The only experimental information on the dehydration of Goosecreekite is given by Dunn *et al.* [21]. They state that placing the sample under vacuum results in a loss of 2.4% mass. The remaining water is lost—12.3% by mass—in two steps, the first between 55 and 222°C and the second at 328°C. Our predicted dehydration profile is in good qualitative agreement—there are clearly three different stages of dehydration. We see that the first two molecules

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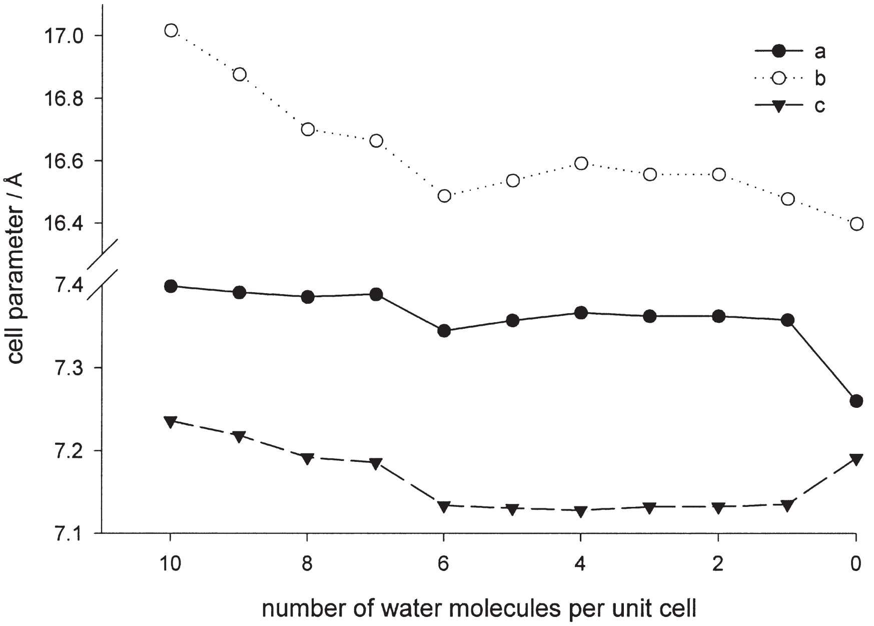

FIG. 5 Predicted changes in unit cell dimensions of Goosecreekite on dehydration.

(corresponding to 2.7% mass) requires the least amount of energy to remove them. This is perhaps expected since it only reduces the coordination number of the Ca^{2+} to 6. The next molecule requires significantly more energy to remove and the last four water molecules have even higher dehydration energies. We are now attempting to confirm these predictions by following the dehydration using *in situ* XRD.

POTENTIAL PARAMETERS AND MINIMISATION METHODS

We have made modification to the potentials in order to facilitate easier energy minimisation. The modifications were restricted to areas of the potential far from equilibrium. That is, the modifications prevent unfeasible structures rather than modify the geometries obtained at minima. The modifications were to the Buckingham potential acting between the T atoms of the framework and the oxygen of the water. In the work of de Leeuw *et al.* [12,13], the cation–water potentials are derived from the cation–lattice oxygen potentials, taking into account the lower charge on the oxygen in water compared to the oxide lattice. Since at the surface, there are near-neighbour interactions between cation and water, these potentials are critical at close range. In the zeolitic environment, the framework oxygens shield the interactions and thus the interactions are more long-range. However, the higher electrostatic contribution of the framework cations requires countering, since in minimisation methods the resulting strong forces can result in the water moving into unfeasible close contact to the framework cations. Thus, an increased repulsive term was required. We therefore used the same values as for the T atom to framework oxygen potential (Si–Ow $A = 1283.907\,\mathrm{eV}$, $\rho = 0.32052\,\text{Å}$ and $C = 10.662\,\mathrm{eV}\text{Å}^6$ and Al–Ow $A = 1460.3\,\mathrm{eV}$, $\rho = 0.29912\,\text{Å}$ and $C = 0.0\,\mathrm{eV}\text{Å}^6$), which have a reasonably strong repulsive term at these closer contacts. We note that at typical cation–water distances in zeolites that the original and the above potential are very similar and differ only at short and therefore unfeasible distances. We also note that the modification will enable molecular dynamics methods to be more easily implemented within these systems since they reduce the "Buckingham catastrophe" which occurs at close contact.

It is clear that the potential parameters used here are suitable and are very capable of reproducing experimental structures of hydrated zeolites. Previous studies have either found difficulty in reproducing experiment [4] or have focussed on systems where the effect of water on the zeolite structure is small, for example Zeolite A [2,3]. Here, we have been able to locate water in both very confined pores and also in larger volumes resulting from removal of water. The potential parameters have successfully been able to describe the geometries and interactions of the intrazeolitic water.

As has been mentioned in the above discussions, obtaining energy minima in these systems has proven non-trivial and time consuming. Perhaps this should be expected given the very complex nature of the potential energy surface. Furthermore, it has become clear how sensitive the minimisation procedure is to the initial configuration. During this work we have experimented with a number of methods of generating the initial water position—here we have been able to use the experimental oxygen position and have only had to consider the orientation of the hydrogen atoms. In systems where the free void space is small, the minimisation algorithms cannot readily rotate molecules given the very high-energy barriers between different orientations. Similarly, there is a multitude of local minima. Thus, it is important to begin with a suitable geometry. Whilst other methods such as Monte Carlo or molecular dynamics could possibly locate minima in a more automated manner they can be expensive, particularly with this model. Furthermore, they would be prone to the same problems encountered with the attraction of water to the highly positive Al and Si atoms, as found above. Thus, we have attempted to develop positioning and minimisation strategies in order, at least, to be able to study static properties.

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One successful method for positioning the hydrogen of the water molecules was to search for minima in the electrostatic potential and place the hydrogen within these minima, subject to suitable constraints on OH bond length and HOH angle. Positioning “by eye” proved less successful as the complex 3-D structure made it very difficult to identify clearly the best position. This was particularly significant in Gismondine where a number of water molecules are only loosely coordinated to the calcium cations. For systems where the oxygen positions are also not known (or at least where not all are known) the problem becomes considerable and careful thought must be given to this problem. Hill *et al*. [4] encountered difficulties in using GCMC with similar materials and others have only considered much lower water loadings [5]. Such methods will find it increasingly difficult to insert water in such small pores and at higher water concentrations. Such problems are further complicated by the rigid framework and fixed cation positions often used in such methods; the results here again highlight the significant framework relaxation and cation motion which occur with changing water content. It is clear that further work is needed to allow the rapid and generalised generation of hydrated zeolite structures.

CONCLUSIONS

Advances are presented in the modelling of hydrated zeolites. We model for the first time small pore zeolites containing strongly coordinated water and highlight how the presence of water influences the distribution of Al within the zeolite framework. The potential models used, and refined here, are shown to be reliable and reproduce remarkably well the intrazeolite water structure and its coordination and interactions with the extra-framework cations and the framework. Work, both experimental and computational, is continuing to study further the dehydration of these materials and also to develop methods for studying the location and motion of water and extra-framework species within the pores.

Acknowledgements

ARRS acknowledges the Royal Society for a Postdoctoral Fellowship and the RSC for a Grant for International Authors. Dr N. de Leeuw is thanked for providing us with the water potentials prior to publication. Dr J D Gale is also thanked for the provision of GULP. We also thank the University of Havana for an Alma Mater Research Grant.

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