Understanding Si/Al distributions in Al-rich zeolites: the role of water in determining the structure of Goosecreekite†

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Inclusion of hydration in atomistic simulations of the zeolite Goosecreekite allowed the determination of the most stable structure, including the distribution of Al in the framework and the position of extra-framework cations and water, and highlight how hydration appears to control the framework distribution.

The increasing use of zeolites in many branches of the chemical industry and, in particular, for environmental pollution control, demands a better understanding of the structure if we are to optimise their application. For catalysis and ion exchange, the number and location of aliovalent atoms in the framework and the charge balancing species govern the performance of a particular material. Thus, being able to determine and understand the location of such species will allow us to produce optimised compositions for specific applications. Whilst diffraction methods can identify extra-framework cation (efc) sites they often do not provide any accurate information on the spatial distribution of framework atoms. Similarly, NMR provides only short-range co-ordination of the framework Al and Si. Thus, whist there are established 'rules' of Al distribution in zeolites—Lowenstein's and Dempsey's rules— there is little further detail available from experiment.[1]

Computational methods, based on interatomic potentials, are well established in modelling the structure of zeolites:[2] for example, demonstrating an energetic basis for Lowenstein's rule.[3] Recently, we have developed a methodology to study the distribution of Al in the frameworks of low and medium Si/Al zeolites.[4–6] Whilst the results obtained are generally in excellent agreement with experimental data on the siting of Al atoms, we find that certain efcs shift away from experimental sites towards the framework – a consequence of the omission of water from our models. We now wish to determine the role of water in controlling both the distribution of Si and Al within the framework and the location of efcs. The limited number of theoretical studies of hydrated zeolites have considered only the location and dynamics[7–10] of water in fixed, ordered or 'random' distributions of Al.

Therefore, as a first step in modelling hydrated zeolites, we consider here the mineral Goosecreekite (IZA code GOO).[11] Experimentally, the material is found to have an ordered Al distribution with a Si/Al of 3, providing a rigorous test of our methodology[4–6] for identifying stable Al distributions. Goosecreekite has a three-dimensional channel structure with a maximum pore opening of 4.7×2.9 Å.

We employ lattice energy minimisation techniques[2] as implemented in the program GULP.[12] For the zeolite and efc interactions we used the potential parameters described by

Jackson and Catlow,[13] while the water related interactions were taken from the work of de Leeuw et al.[14,15] These water potentials were originally derived for modelling of solvation at ionic mineral surfaces (e.g. $CaCO_3$). 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 the modelling of proteins and other biomolecules. They include a description of polarisation, which will be significant.

The Goosecreekite unit cell ($Ca_2Al_4Si_{12}O_{32}$) comprises eight unique tetrahedral sites,[11] each with a multiplicity of two. Six of the sites are found to be occupied by Si (labelled Si1, Si2,…Si6), the remaining two sites by Al (Al1 and Al2). We therefore considered a total of 1820 different framework configurations at the outset, with four Al distributed over the 16 sites. On the basis of our previous work[4–6] we applied Lowenstein's rule and eliminated those related by symmetry elements of the experimental[11] space group $P2_1$, reducing the number of structures considered to 89.

For the resulting minimised structures we calculated a Boltzmann distribution probability (Table 1) at 600 K, which is typical for volcanic mineral formation. We find that the most stable calculated configuration (C1§) possesses an ordered Al distribution, but that the Al is at the sites labelled Si3 and Si4. The second most stable configuration, C2, (Fig. 1) does have the experimental Al distribution, but is significantly less stable. We also find significant differences in the location of the efc sites.

Table 1 The calculated most stable configurations for Goosecreekite without water. Those configurations (of the 89 considered) with a Boltzmann population (*P*) greater than 5% at 600 K are shown

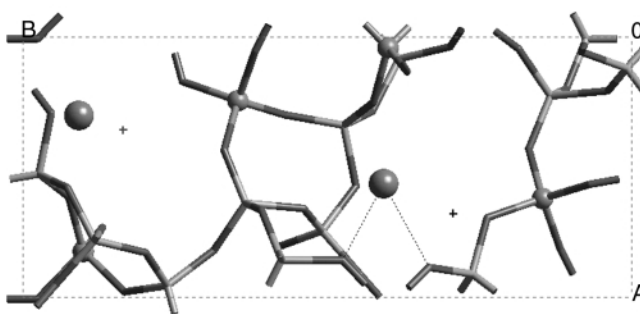| Configuration	E_{latt} per u.c./eV	P (%)	Al location
C1	−1936.389	53.2	2 at Si3, 2 at Si4
C2	−1936.345	22.5	2 at Al1, 2 at Al2
C3	−1936.308	11.0	Si1, Si3, Si4, Al1
C4	−1936.285	7.1	Si3, Si6, Al1, Al2

Fig. 1 The second most stable calculated structure (C2) of Goosecreekite without water. The Al (spheres in framework) is located at the experimentally found sites. The Ca^{2+} are two-fold co-ordinated to the framework and are significantly displaced from the experimental sites (black crosses).

Table 2 The unit cell parameters for the two most stable calculated structures, with and without water, are given and compared with experiment. For each structure the cell angle α and γ are calculated to be 90.00°. Experimentally, $\alpha = \gamma = 90°$

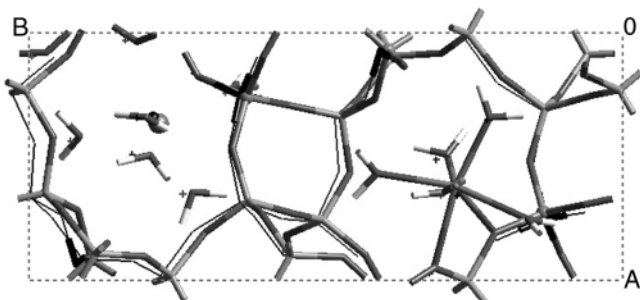|	E_{latt} per u.c./eV	a/Å	b/Å	c/Å	β/°	V/Å^3
Expt.[11]		7.401	17.439	7.293	105.44	907.3
C1 (dehyd.)	−1936.389	7.358	16.124	7.092	110.31	853.5
C2 (dehyd.)	−1936.345	7.409	17.036	7.155	109.10	789.1
C1 (hyd.)	−2036.357	7.385	16.855	7.211	108.17	852.9
C2 (hyd.)	−2036.598	7.398	17.017	7.236	106.38	874.0

Fig. 2 The most stable calculated structure of Goosecreekite with water (C2) and the experimental unit cell (thin black lines with Al highlighted as tubes). Highlighted in the right channel is the co-ordination sphere of the Ca^{2+}. Also shown in the left channel are the experimental water oxygen (black crosses) and Ca^{2+} (black sphere) positions for comparison to the calculated sites (tubular water and larger spheres).

In the most stable calculated configuration, C1, we find that the Ca^{2+} are located along a, which are not observed experimentally, and coordinate strongly to four framework oxygens. Conversely, in C2 the Ca^{2+} are located close to the experimental sites in the channel along [001]. However, these cations can coordinate to only two framework oxygen atoms. We also note the reduced lattice parameters (Table 2) compared with experiment.

Although our methodology has successfully identified stable configurations that are indeed very similar to experiment, notable differences remain. In particular, the experimental framework structure is not sufficiently stabilised by the dehydrated cations (in the calculation) and as a consequence is not the most stable configuration calculated. It is also clear that there is considerable interplay between the location of Al and the siting of the efc sites. Thus, we now need to consider whether the omission of water from these calculations is significant and responsible for the observed discrepancies.

We placed 10 water molecules[11] in the unit cells of C1 and C2 and re-optimised the structures. On energy minimisation, we now find that C2 is more stable than C1 by 0.32 eV per unit cell (Table 2). Furthermore, the calculated structure is now in even better agreement with experiment (Fig. 2, Table 2), with a discrepancy of only 3.6% in the cell volume.

The cations in the calculated, hydrated C2 structure are now located very close to the experimental sites, being 7-fold co-ordinated to five H$_2$O and two framework oxygens (Fig. 2), as in experiment.[11] Whilst the position and co-ordination of Ca^{2+} in C1 are also in good agreement with experiment, the efcs are

more distant from the AlO$_4$ tetrahedra, which destabilises this particular Al distribution. Thus, the role of water in influencing the Si/Al distribution in this zeolite can be considered as a combination of both electrostatic—screening the electrostatic interaction between the efc and the framework—and steric factors—preventing the efcs from occupying the smaller channels. These effects are reflected in the changes in cell volume (Table 2). A dramatic increase is seen in the cell volume of C2 upon hydration, where water screens the electrostatics and also occupies the same channels as the efcs. For C1, in contrast, the efcs are in the small channels in the dehydrated structure, whilst they move into the larger channels on hydration, resulting in only a small overall change in cell volume.

Our results show how, once solvation is considered, our methodologies and models are able to identify stable Si/Al distributions as well as reproducing the extra-framework structure of both cations and water. Agreement with the experimental structure is excellent. The work clearly demonstrates how water is critical, not only in stabilising the structure but also in actually determining the position of efc sites and framework Al distributions. The successful reproduction of the extra-framework structure also shows that the water potentials of de Leeuw et al.[14,15] are suitable for simulations of hydrated zeolites. Further evaluation of the water potential is underway, as are studies of cation exchange.

Notes and references

§ The structure of C1 with and without water and a further illustration of the experimental structure are provided as ESI†.

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