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Optimized hydrogen positions for aluminium and iron containing hydroxide minerals

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Abstract The structures of a number of hydroxide and oxyhydroxide minerals have previously been reported without the hydrogen positions explicitly defined. Here we use two atomic scale computer simulation techniques, one based on classical ionic potentials, the other on density functional theory (DFT), to predict these positions. The aim is not only to provide data that can be used as the basis for future experimental structure optimizations but also model parameters that can be used to predict complex hydroxide structures. The efficacy of the approach is demonstrated through the comparison of predicted and experimental data for minerals whose hydrogen positions are known.

Introduction

It can be very difficult to use X-ray diffraction methods to locate hydrogen atom positions because hydrogen only weakly scatters X-rays. Neutron diffraction methods are more reliable in this regard, however, they have only been used to determine a few hydroxide and oxyhydroxide mineral structures. This is unfortunate because knowledge of hydrogen positions is necessary to understand, for example, how interlayer hydrogen bonding is achieved. A further complication is that often the hydrogen atoms exhibit a degree of positional disorder, which results in refinements that require partial occupancy of sites [1].

Where experimental data is not available, as an alternative it is possible to predict the structure of minerals using energy minimization techniques [2, 3]. Here using methods based on a transferable ionic potential model [4] the hydrogen positions of goethite α-FeO(OH), β-FeO(OH), δ-AlO(OH), gibbsite $Al(OH)_3$, nordstrandite $Al(OH)_3$, and bernalite $Fe(OH)_3$ will be predicted. In a recent study Chroneos et al. [4] showed that this new potential model could accurately describe the lattice parameters and cation positions of these phases together with other hydroxide and oxyhydroxide materials. The present study extends the analysis by focusing on hydrogen positions. The results are further tested by comparing to equivalent calculations, based on a density functional approach, for all the aluminium containing minerals. Density functional calculations have previously been used to successfully investigate the complexities of hydrogen in γ-Al_2O_3 [5]. A further aim is to develop effective potential models that can be used to simulate complex mineral interfacial structures that are currently beyond the reach of quantum mechanical approaches.

Experimental data

The structures of all the mineral phases described below were determined using X-ray diffraction

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techniques and consequently definitive hydrogen positions were not reported.

Suzuki et al. [6] determined the new phase δ-AlO(OH) (space group $P2_1nm$ No. 31), which was synthesized at 21 GPa and 1,000 °C. In that study Suzuki et al. [6] applied the β-CrO(OH) (guyanaite) model of Christensen et al. [7], derived using powder neutron diffraction, that identified two possible space groups Pnnm and $P2_1nm$. Subsequently Tsuchiya et al. [8] using density functional calculations proposed three possible and stable structures with space group Pnnm, $P2_1nm$ and $Pn2_1m$ for δ-AlO(OH) but did not report hydrogen positions explicitly. These prompted further experimental work by Kudoh et al. [9], which determined the space group to be Pnn2, a non-centrosymmetric subgroup of Pnnm.

Goethite, α-FeO(OH), is orthorhombic (space group Pnma No. 62) [10] and is isostructural with CrO(OH) (bracewellite), AlO(OH) (diaspore) and ScO(OH). For the latter two structures hydrogen positions are known and therefore provide a starting point for these calculations. Goethite is the most stable iron oxyhydroxide [11] and consists of double bands of octahedra, which are linked by corner sharing to form 2 × 1 tunnels.

The crystallography, physical and chemical properties of akaganeite, β-FeO(OH), are controversial despite the significant number of experimental structural investigations. Akaganeite was initially described as tetragonal (space group I4/m No. 87) [12, 13] but subsequently as monoclinic (space group I2/m No. 12) [14]. The monoclinic akaganeite structure was further refined using neutron powder diffraction [15] which concluded that structural tunnel sites were partially occupied by Cl^- ions. These experimental investigations were consistent with the concept that Cl^- ions are necessary for the formation and stabilization of the akaganeite structure. Conversely, other studies [16] have shown that Cl^- ions can be substituted by hydroxyl groups without loss of stability and that in certain circumstances (for example weathering of meteorites) akaganeite will initially form with hydroxyl groups occupying the tunnel sites [17]. Recently, Garcia et al. [18] also reported akaganeite as monoclinic (space group C2/m No. 12), they did not, however, publish the fractional coordinates.

Bernalite, $Fe(OH)_3$, was first described as orthorhombic, space group Immm No. 71 [19], which resembles the distorted perovskite structure of the rare earth orthoferrites [20]. Recently, Welch et al. [21] also reported bernalite as orthorhombic but with space group Pmmn. This latter structure closely resembles that of $FeGe(OH)_6$. Bernalite is unstable and commonly coexists with goethite, which is its decomposition product [19, 20].

Saalfeld and Wedde [22] described the gibbsite structure, $Al(OH)_3$, with space group $P2_1/n$ No. 14. Gibbsite exhibits the same stoichiometry as its polymorph bayerite and has a similar layered structure [23]. Fleming et al. [24] have determined the hydrogen fractional coordinates of gibbsite using density functional techniques. Here we will compare those results with predictions based on our pair potential approach.

Bosmans [25] calculated the structural coordinates of Nordstrandite $Al(OH)_3$ (space group No. 2), a synthetic aluminium hydroxide that had been initially identified by van Nordstrand et al. [26].

Computational details

Classically based simulation technique

This study is based on the classical Born model description of the lattice [27]. Thus, the interaction between a pair of ions, $E(r_{ij})$, is given by,

$$E(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

where the first term is the Coulomb interaction between a pair of ions, the second term represents the short range repulsive interaction and the third term is van der Waals energy. In this equation r_{ij} is the separation between ions i and j; A_{ij}, ρ_{ij} and C_{ij} are adjustable parameters specific to the given pair of ions. It is important to appreciate that a single set of potentials has been derived to model all these structures in order to support further studies of more complex systems in future.

In all cases a single unit cell is repeated periodically through space. The Coulombic forces are summed using Ewald's method [28], whereas the short-range forces are summed explicitly up to a cut-off value of 20 Å. For a given set of parameters, the lattice parameters and positions of ions within the unit cells are identified through energy minimization. The parameters were selected by fitting to an extensive set of hydroxides, oxyhydroxides and oxide structures [4]. The code GULP [29] was used for all simulations.

Quantum mechanically based simulation technique

These calculations are also based on a model that assumes a single unit cell is repeated throughout space.

However, forces are generated at the density functional level [30] using the generalized gradient approximation (GGA) of Perdew and Wang [31]. The k-point set used is based on a Monkhorst-Pack grid, which gives an approximate k-point separation of 0.04 Å^{-1} for all structures. The plane wave basis set was expanded to a cut-off of 650 eV in conjunction with ultra-soft pseudopotentials. The simulations were performed under constant pressure conditions so that the unit cell parameters, cation, oxygen and hydrogen fractional coordinates were allowed to relax using energy minimization. Consequently the calculations were performed at the static limit. The package CASTEP was used for all the DFT calculations [32, 33].

Results and discussion

Comparison with known hydrogen positions

As evidence of the efficacy of the model, the predicted hydrogen fractional coordinates of diaspore, AlO(OH) are reported in Table 1, together with the known experimental data [34] and previous predictions [35] using the local density approximation (LDA) quantum mechanical technique. For these, the aluminium–oxygen and hydrogen–oxygen distances were presented previously [4].

In Table 2 the predicted hydrogen fractional coordinates of gibbsite, $Al(OH)_3$, are compared to those derived by Fleming et al. [24] using a LDA quantum mechanical technique. From these results and those in Table 1 it is clear that the simulations based on pair potentials are capable of reproducing both structures of hydroxide containing minerals and their hydrogen positions. Consequently this approach can be used to study hydroxide and oxyhydroxide materials for which the experimental data is incomplete.

Table 1 The predicted lattice parameters and fractional coordinates using a classical simulation technique compared with previous DFT predictions* [34] and the experimentally derived structure of diaspore AlO(OH) [33] for space group Pnma

Space group Pnma Diaspore AlO(OH)

	Classical	DFT	Experimental
a (Å)	4.367	4.401	4.401
b (Å)	9.291	9.421	9.425
c (Å)	2.941	2.845	2.845
Al(x)	0.037	0.045	0.045
Al(y)	0.850	0.856	0.855
Al(z)	0.250	0.250	0.250
O1(x)	0.755	0.711	0.712
O1(y)	0.213	0.199	0.199
O1(z)	0.250	0.250	0.250
O2(x)	0.209	0.194	0.197
O2(y)	0.043	0.053	0.053
O2(z)	0.250	0.250	0.250
H1(x)	0.423	0.415	0.410
H1(y)	0.072	0.089	0.088
H1(z)	0.250	0.250	0.250

* This author kept the lattice parameters fixed at the experimental values and only allowed the internal parameters to vary

Table 2 Atomistic simulation and quantum mechanically derived [23] hydrogen fractional coordinates in gibbsite $Al(OH)_3$

	Classical	DFT
H1(x)	0.081	0.077
H1(y)	0.138	0.137
H1(z)	0.845	0.874
H2(x)	0.572	0.575
H2(y)	0.565	0.552
H2(z)	0.879	0.897
H3(x)	0.496	0.494
H3(y)	0.116	0.111
H3(z)	0.783	0.795
H4(x)	0.956	0.951
H4(y)	0.813	0.815
H4(z)	0.864	0.887
H5(x)	0.294	0.296
H5(y)	0.715	0.717
H5(z)	0.780	0.794
H6(x)	0.807	0.806
H6(y)	0.167	0.161
H6(z)	0.785	0.798

Predicted hydrogen positions

The classically derived atomic fractional coordinates of nordstrandite, δ-AlO(OH), goethite, akaganeite and bernalite are reported in Table 3. No hydrogen positions have previously been reported for these minerals. From the data in these tables it is clear that the models reproduce the lattice parameters, the cation and oxygen positions to a degree of accuracy that makes the predicted hydrogen positions potentially useful. This is not surprising as the pair potentials were derived by fitting to an extensive range of hydroxides, oxyhydroxides and their corresponding oxides to enhance model transferability.

By way of comparison, results for nordstrandite (Table 3, panel A) and δ-AlO(OH) (Table 3, panel B) were derived using the DFT approach. These results also generally reproduce the experimental data. Interestingly where there is disagreement between experiment and the two modeling techniques, the difference is by no means consistent for both models (see below for more details). Nevertheless, the predicted pair potential hydrogen positions are in good agreement with the two predicted DFT derived structures.

Table 3 Predicted and experimentally derived (**a**) nordstrandite $Al(OH)_3$ [24] lattice parameters, angles and fractional atomic coordinates for space group $P\bar{1}$, (**b**) δ-AlO(OH) [5] lattice parameters and fractional atomic coordinates for space group $P2_1nm$, (**c**) goethite α-FeO(OH) [9] lattice parameters and fractional atomic coordinates for space group Pnma, (**d**) [11] lattice parameters and fractional atomic coordinates for akaganeite β-FeO(OH), (**e**) bernalite $Fe(OH)_3$ [20] lattice parameters and fractional atomic coordinates for space group Pmmn

	Classical	DFT	Experimental
(**a**) Space group $P\bar{1}$ Nordstrandite $Al(OH)_3$			
a (Å)	5.089	5.161	5.082
b (Å)	5.049	5.197	5.127
c (Å)	5.002	4.869	4.980
α (°)	96.46	99.07	93.66
β (°)	120.09	119.78	118.92
γ (°)	67.64	66.88	70.27
Al(x)	0.672	0.679	0.670
Al(y)	0.010	0.000	0.010
Al(z)	0.337	0.342	0.337
O1(x)	0.276	0.281	0.252
O1(y)	0.223	0.216	0.242
O1(z)	0.344	0.353	0.319
O2(x)	0.524	0.519	0.534
O2(y)	0.225	0.212	0.203
O2(z)	0.974	0.979	0.943
O3(x)	0.903	0.913	0.908
O3(y)	0.226	0.207	0.208
O3(z)	0.601	0.628	0.622
H1(x)	0.181	0.169	–
H1(y)	0.568	0.585	–
H1(z)	0.392	0.389	–
H2(x)	0.079	0.116	–
H2(y)	0.275	0.221	–
H2(z)	0.144	0.133	–
H3(x)	0.589	0.622	–
H3(y)	0.362	0.317	–
H3(z)	0.935	0.946	–
(**b**) Space group $P2_1nm$ δ-AlO(OH)			
a (Å)	2.890	2.793	2.833
b (Å)	4.323	4.198	4.224
c (Å)	4.546	4.686	4.713
Al(x)	0.000	0.000	0.000
Al(y)	0.290	0.277	0.274
Al(z)	0.000	0.011	0.000
O1(x)	0.000	0.000	0.000
O1(y)	0.987	0.996	0.993
O1(z)	0.344	0.370	0.359
O2(x)	0.000	0.000	0.000
O2(y)	0.520	0.500	0.491
O2(z)	0.670	0.671	0.664
H(x)	0.000	0.000	–
H(y)	0.180	0.196	–
H(z)	0.476	0.499	–
(**c**) Space group Pnma Goethite α-FeO(OH)			
a (Å)	4.577		4.619
b (Å)	9.791		9.953
c (Å)	3.138		3.024
Fe(x)	0.061		0.047
Fe(y)	0.850		0.855
Fe(z)	0.250		0.250
O1(x)	0.725		0.714
O1(y)	0.207		0.201
O1(z)	0.250		0.250
O2(x)	0.195		0.192
O2(y)	0.051		0.052
O2(z)	0.250		0.250
H(x)	0.400		–
H(y)	0.080		–
H(z)	0.250		–
(**d**) Space group I4/m Akaganeite β-FeO(OH)			
a (Å)	10.295		10.480
b (Å)	10.295		10.480
c (Å)	3.126		3.023
Fe(x)	0.352		0.348
Fe(y)	0.144		0.167
Fe(z)	0.000		0.000
O1(x)	0.160		0.153
O1(y)	0.208		0.180
O1(z)	0.000		0.000
O2(x)	0.535		0.542
O2(y)	0.165		0.167
O2(z)	0.000		0.000
H1(x)	0.086		–
H1(y)	0.153		–
H1(z)	0.000		–
(**e**) Space group Pmmn Bernalite $Fe(OH)_3$			
a (Å)	7.745		7.619
b (Å)	7.700		7.619
c (Å)	7.503		7.553
Fe1(x)	0.250		0.250
Fe1(y)	0.250		0.250
Fe1(z)	0.000		0.000
Fe2(x)	0.750		0.750
Fe2(y)	0.750		0.750
Fe2(z)	0.500		0.500
O1(x)	0.500		0.500
O1(y)	0.273		0.318
O1(z)	0.564		0.558
O2(x)	0.000		0.000
O2(y)	0.752		0.678
O2(z)	0.064		0.058
O3(x)	0.194		0.195
O3(y)	0.191		0.190
O3(z)	0.751		0.750
O4(x)	0.239		0.178
O4(y)	0.500		0.500
O4(z)	0.571		0.573
O5(x)	0.722		0.818
O5(y)	0.000		0.000
O5(z)	0.071		0.073
H1(x)	0.500		–
H1(y)	0.379		–
H1(z)	0.639		–
H2(x)	0.000		–
H2(y)	0.714		–
H2(z)	0.191		–
H3(x)	0.104		–
H3(y)	0.106		–
H3(z)	0.747		–

Table 3 continued

	Classical	DFT	Experimental
H4(x)	0.237		–
H4(y)	0.500		–
H4(z)	0.704		–
H5(x)	0.605		–
H5(y)	0.000		–
H5(z)	0.122		–

Table 4 Predicted and experimentally derived cation–oxygen distances (Å) for the hydroxide minerals considered

	Classical	DFT	Experimental
Nordstrandite	1.89	1.94	2.01*
δ-AlO(OH)	1.80–2.08	1.76–2.12	1.83–2.03*
Goethite	1.92–2.18	–	1.95–2.09*
Akaganeite	1.90–2.19	–	2.01–2.20*
Bernalite	2.01	–	2.04

* These distances were calculated here from the published atomic coordinates

It should be stressed that where differences between the experimental and computationally derived cell parameters exist these do not translate into significant errors in bond lengths (Table 4). That is, the derived ranges of cation–oxygen distances for the hydroxide and oxyhydroxides minerals are within the experimentally observed ranges (Note: for the classical model distances are calculated between the oxygen core and cation).

Aluminium hydroxides

The crystal structure of nordstrandite is reproduced by both atomistic simulation techniques. Nevertheless, for most lattice parameters, angles and fractional coordinates the classical ionic model is in better agreement with the experimental results. The predicted hydrogen positions are consistent for both techniques.

With δ-AlO(OH), both the classical and DFT energy minimization calculations lead only to the $P2_1nm$ crystal structure [6]. Other space groups previously suggested are not stable. Again, the hydrogen fractional coordinates determined by the two computational techniques are in good agreement and both also predict structural parameters in correspondence with experimental data.

Iron hydroxides

The structure of goethite is well established. The pair potentials simulations yield a structure that is stable with respect to energy minimization (Table 3, panel C) and reproduces the experimental unit cell volume to within 1.15%. It should be noted that the predicted fractional hydrogen coordinates of goethite are in excellent agreement with the fractional hydrogen coordinates of its isostructural diaspore (Table 1).

As discussed previously, in the presence of Cl^- ions, akaganeite has been reported as monoclinic, but this is beyond the scope of the present work. Therefore, here only the tetragonal structure was modelled [11]. The classical model results are in good agreement with the experimental values (Table 3, panel D), with the predicted volume underestimated by only 0.21%.

The Pmmn orthorhombic structure of bernalite [21] was stable with respect to energy minimization via the classical simulation technique. The pair potential technique reproduced the experimental lattice parameters, cation and oxygen fractional coordinates to a degree of accuracy that makes the model useful in predicting hydrogen positions (Table 3, panel E).

Conclusions

The combination of classical and DFT based energy minimization simulations can be used to provide hydrogen fractional coordinates for mineral systems where experimental data is presently lacking. These then offer suitable starting models for the analysis of experimental diffraction data. The agreement between the predictions made using the classical model and both the experimental data and the quantum mechanical based simulations provides confidence in the future use of the more simple approach to model complex minerals and intergrowth or interface structures.

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