

LETTER

A first-principles determination of the orientation of H_3O^+ in hydronium alunite

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ABSTRACT

The existence or otherwise of the hydronium cation within the mineral alunite has proved difficult to verify based on experimental data alone. In the present study, we employ first-principles quantum mechanical techniques to determine the nature of the structure of hydronium alunite. A new model for the hydrogen atom disorder is predicted that differs from a proposed arrangement in the case of the analogous stoichiometric hydronium jarosite. Instead of occupying one of two orientations that respect the threefold symmetry axis passing through the oxygen, the cation is found to occupy a tilted orientation leading to a greater degree of disorder. Dynamical simulations indicate that the reorientation of the hydronium ions is rapid and exhibits no correlation between the cation sites. The higher level of disorder in the hydrogen positions offers an explanation as to why their location has proved elusive thus far.

Keywords: Alunite, hydronium, density functional theory, simulation

INTRODUCTION

Minerals of the alunite supergroup are widely distributed and play significant roles in the storage and release of water, acidity, and toxic elements such as As and Pb. Members of the supergroup form in a diverse range of terrestrial environments and have also been identified on Mars, providing mineralogical evidence that the planet was once wet and may have supported life (Klingelhöfer et al. 2004). Alunite forms as the result of the dissolution of aluminosilicates or aluminum oxides in weathering under acidic conditions, in the presence of a sufficient source of sulfur, where it can form large deposits such as those in Tolfa, Italy. Formation in lacustrine and hydrothermal environments is also known (Stoffregen and Alpers 1992; Bigham and Nordstrom 2000; Stoffregen et al. 2000).

The isostructural alunite supergroup has a general formula of $\text{AB}_3(\text{TO}_4)_2(\text{OH})_6$, where A represents cations with a coordination number ≥ 9 , and B and T represent cation sites with octahedral (O) and tetrahedral (T) coordination, respectively (Jambor 1999). In the parent mineral, alunite $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$, the B-site cation is Al^{3+} , the A site is occupied by K^+ in 12-fold coordination, and the T site is filled by sulfur leading to the formation of what can be considered to be a sulfate anion (SO_4^{2-}). Some substitution by other cations (e.g., Na for K) is found in the structure, but impurities are much less common than in the isostructural jarosite phases. The alunite structure often contains A- and B-site vacancies (Dutrizac and Jambor 2000; Greedan 2001), and “excess”, non-OH water, which is assumed to be in the form of hydronium (or “oxonium,” H_3O^+) that substitutes for K^+ on the A site (Ripmeester et al. 1986; Alpers et al. 1989). As Lager et al. (2001) point out, the existence of hydronium is supported

by K^+ deficiencies in the structure and the fact that hydronium alunite end-members without any alkalis can be synthesized (Murphy et al. 2009).

As hydronium cannot be detected using standard techniques, such as electron microprobe analysis, many researchers have attempted to prove its existence in the alunite or jarosite structure using vibrational, NMR, and other spectroscopic methods (Ripmeester et al. 1986; Breitingner et al. 1997; Lager et al. 2001; Nielsen et al. 2007, 2008 and references therein). Despite all of this effort, uncertainty regarding the nature and precise orientation of hydronium in alunite still exists. Nielsen et al. (2007) found that H_3O^+ is stable in the alunite structure only for near stoichiometric materials, with the presence of B-site vacancies leading to reaction of hydronium with the adjacent hydroxyl groups. This finding is similar to that proposed for hydronium jarosite by Grohol et al. (2003). Using incoherent, inelastic neutron-scattering methods, Lager et al. (2001) were unable to distinguish hydronium from OH groups and H-bonded H_2O molecules in alunite, and suggested that non-OH H_2O be characterized by analyzing neutron, optical and NMR data by “rigorous numerical simulations.” We follow this recommendation and present herein the results of quantum mechanical calculations aimed at understanding the nature of hydronium in the alunite structure.

EXPERIMENTAL METHODS

Periodic density functional theory within the Kohn-Sham formalism has been employed to study the structure and properties of hydronium alunite. Specifically, we use the particular numerical implementation contained within the SIESTA methodology and code (Soler et al. 2002). Here the nuclei and core electrons of atoms are represented through the use of norm-conserving pseudopotentials of the modified Troullier-Martins form (Troullier and Martins 1991), while the valence electrons are treated explicitly. The Kohn-Sham states are expanded in a basis set consisting of the numerical pseudo-atomic orbitals (PAOs) that are strictly confined

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within a given radius through the introduction of a soft-confining potential. These PAOs are divided into multiple components to improve the transferability of the basis set between different chemical environments. Here we use a basis set of triple-zeta, doubly polarized quality (TZ2P) for oxygen and hydrogen, while sulfur and aluminum are described using a double-zeta polarized (DZP) basis. In calculating quantities that depend on the electron density, such as the exchange-correlation functional, an auxiliary basis set is exploited consisting of a Cartesian grid for which a cut-off of 800 Ry or 400 Ry was chosen according to whether semi-core states are included for aluminum or omitted, respectively. The Brillouin zone was sampled using a Monkhorst-Pack mesh whose fineness was controlled using the K-grid cut-off (Moreno and Soler 1992) with a value of 12 \AA .

Two density functionals have been explored in the current work. Initially, all calculations were performed with the generalized gradient approximation (GGA) due to Perdew, Burke and Ernzerhof (PBE) (Perdew et al. 1996), which has been widely employed for solid-state calculations. Over the last few years, several new functionals have been derived that appear to exhibit improved performance for the structures and energies of solids, while retaining the computational expediency of GGA functionals. Here we have also performed the structural optimizations using the AM05 functional (Armiento and Mattsson 2005) since not only does this work well for condensed phases, but it also offers a relative accurate description of the water dimer (Mattsson and Mattsson 2009), thus suggesting it will be a reliable functional for the study of hydronium alunite.

An initial model for hydronium alunite was constructed based on recent single-crystal X-ray data for hydronium jarosite (Majzlan et al. 2004) in which iron was replaced by aluminum. While the positions of the hydroxyl group hydrogen atoms were refined in this structure, the locations of the atoms within the supposed hydronium ion, other than oxygen, remain unknown. In the case of hydronium jarosite, Basciano and Peterson (2007) have proposed that the threefold rotational axis of the cation is parallel to the c -axis of the hexagonal cell to be consistent with the site symmetry of the O atom. In their work, it is suggested that the protons of the hydronium ion are disordered over two orientations in which they are situated either above or below the oxygen along the c -axis so as to form three equal hydrogen bonds to the neighboring O atoms of the sulfate groups (Fig. 1). This orientation also appears in Figure 1 of Nielsen et al. (2007), though it is important to note that this manuscript does not attach any significance to the orientation shown. Each unit cell contains three hydronium ions and so, given that we are constrained to consider ordered structures, an initial configuration has been chosen with two hydroniums oriented in one direction and the third in the opposing sense. In the present work, we only consider the case of stoichiometric hydronium alunite, and therefore the stability of H_3O^+ in the presence of B-site vacancies is deferred for future work.

Having created an initial structural model for hydronium alunite, it is important to explore the potential energy surface for this system as extensively as possible. First of all, the structure is energy minimized at constant volume and then subsequently the unit cell is also relaxed. To ensure that a valid minimum has been achieved, the phonon spectrum is then computed for this structure. Of course, given the relative high mobility of protons within many systems, it is important to determine whether the optimized structure is only a local minimum or not by more widely probing the potential energy surface. To this end, first-principles molecular dynamics has been conducted in the NPT ensemble at 298 K using a Nosé thermostat. Two separate runs have been performed; the first one employed a single unit cell with a time step of 0.25 fs and was run for a total time of 2 ps, while the second simulation is for a larger $2 \times 2 \times 1$ supercell containing 348 atoms and using a longer time step of 0.5 fs for a total of 0.5 ps. Atomic masses for H, O, S, and Al were 1.0078, 16.0, 26.98, and 32.06 a.u., respectively.

RESULTS AND DISCUSSION

The optimized structure of hydronium alunite, based on the initial trial configuration, is illustrated in Figure 2. During the relaxation of the structure, the orientation of hydronium has significantly changed and adopts a very different configuration to that proposed by Basciano and Peterson (2007) for hydronium jarosite in which the threefold rotational symmetry of both the isolated hydronium ion and the cation A-site are aligned. Instead it is found that hydronium prefers to rotate such that the plane of the three hydrogen atoms is closer to being parallel to the c -axis than to the a - b plane of the hexagonal unit cell (see Fig. 2). When adopting this lower symmetry tilted orientation, the hydronium cation is still able to form three hydrogen bonds, but

two are to the bridging hydroxyl groups, while only the third is to an O atom of a sulfate anion. From this, we can deduce that the energetic driver for the change in orientation must be the lower strength of the hydrogen bond to the sulfate anion than to a hydroxyl group. The distribution of hydrogen bond dis-

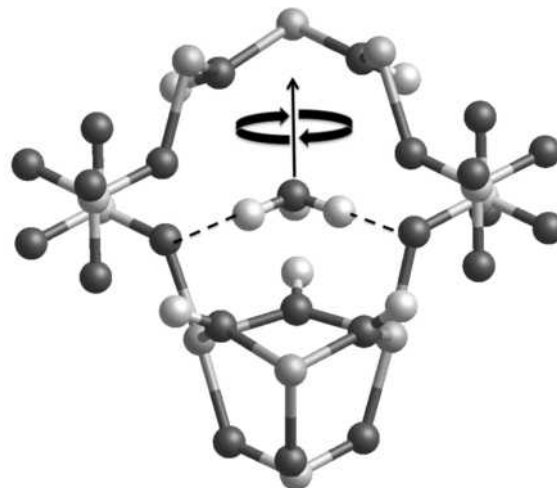


FIGURE 1. Proposed literature orientation of H_3O^+ in hydronium jarosite (Basciano and Peterson 2007), adapted for hydronium alunite, illustrating the local geometry about the cation. The vertical arrow indicates the rotational axis of symmetry, parallel to the c axis of the crystal structure, passing through the O atom of the hydronium (H_3O^+) ion. Dashed lines indicate two of the three hydrogen bonds to the O atoms of sulfate bonded to the aluminum atom. A third equivalent hydrogen bond exists going back into the plane of the figure (not shown for clarity). This configuration represents one of two degenerate orientations, where the second possibility corresponds to reflection in the a - b plane passing through the oxygen of hydronium.

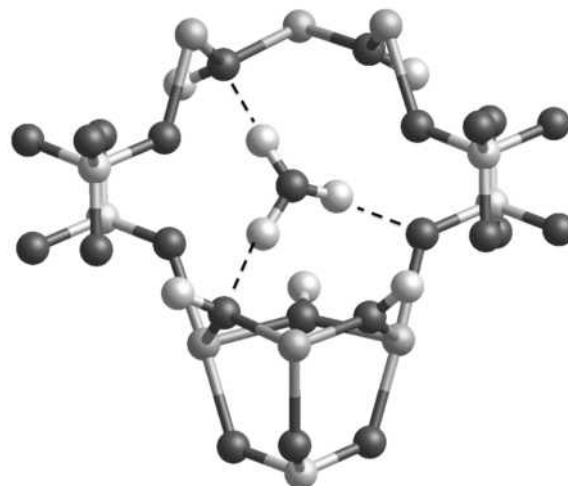


FIGURE 2. Optimized structure of the hydronium cation within the alunite structure as computed at the AM05/TZ2P level of theory. Here the orientation of the figure is the same as shown in Figure 1, with the c axis being vertical as shown. The hydronium cation now forms two hydrogen bonds to O atoms of hydroxyl groups that bridge aluminum atoms (on left-hand side of figure) and one hydrogen bond to an O atom of a sulfate group coordinated to another aluminum atom (right-hand side).

tances for the H··OH and H··OSO₃ interactions are 1.550–1.664 (1.611–1.720) and 1.818–1.854 (1.875–1.901) Å, respectively, where the values are for the AM05 functional, while those for the PBE functional are given in parentheses. Consequently, the distances support the premise that the hydrogen bonds to the hydroxyl groups are stronger. While in theory it would be possible to form three hydrogen bonds from hydronium to hydroxyl groups, this would involve a considerable displacement of the ion from the center of the A-cation site parallel to the *c*-axis and so this appears to be disfavored for other reasons, besides being inconsistent with the known oxygen position from X-ray diffraction. The cell parameters and coordinates for the optimized material at the AM05 level are provided as supplementary information (in three different formats) to allow the reader to fully view the structure¹.

By preferring to adopt a tilted orientation, the hydronium cation is able to occupy 12 distinct configurations within each A site with the same combination of hydrogen bonds, rather than just the two that would be possible based on the Basciano and Peterson model. Not only does this lead to a greater entropic stabilization, but also explains why the level of hydrogen (and by implication deuterium) disorder is so high that these atoms have yet to be located in diffraction studies, unlike the protons of the hydroxyl groups.

Having obtained an initial optimized structure for hydronium alunite, it is important to test whether this is both stable and representative. To address the question of whether this structure is a genuine minimum, the phonon frequencies have been determined for the gamma point. No imaginary modes were present in the spectrum, thus confirming the structure to be at least locally stable. Analysis of the vibrations allows the modes associated with the presence of the hydronium ion to be identified. While a large number of bands associated with stretching of the hydroxyl modes are between 3460 and 3573 cm⁻¹, the modes for H₃O⁺ lie at lower frequencies, as described below. Three modes between 3422 and 3436 cm⁻¹ are predominantly due to the hydroxyl groups, but with some coupling to the hydronium, while the main stretching vibrations of this cation lie over the broad range of 2573–3412 cm⁻¹, though with most of the frequencies being weighted toward the upper end of this region. Inelastic neutron scattering (INS) reveals that there is a notable change in intensity in the band around 3500 cm⁻¹ (Lager et al. 2001), which is broadly consistent with the present results when allowing for the likely systematic red-shift in the calculated frequencies arising from the overestimation of the cell volume [732.2 Å³ calculated vs. 727.6 Å³ experiment (Lager et al. 2001)]. Grohol et al. (2003) also attribute the presence of a broad peak at 3400 cm⁻¹ as being due to the hydronium ion for the analogous case of jarosite, in accord with our observations for alunite. INS results indicate the emergence of a sharp peak close to 1648 cm⁻¹ in the hydronium alunite, relative to the parent material. In the calculated phonon spectrum, two sharp bands at 1602 and 1627 cm⁻¹ consist of three

modes each, which correspond to the almost pure bending modes of hydronium. These modes represent the best evidence that the experimental INS spectrum is consistent with the existence of H₃O⁺, though it cannot be considered conclusive in itself. Lower frequency modes of the hydronium ion, such as umbrella inversion, are found to be strongly coupled to other lattice modes and therefore do not lend themselves to diagnostic use.

While the evidence from the phonon spectrum proves that the model structure for hydronium is stable, this does not preclude the possibility that this is a local minimum that is unrepresentative. To explore the wider potential energy surface for hydronium alunite first-principles molecular dynamics has been performed for both a single cell and 2 × 2 × 1 supercell. The results for both simulations are similar and so only the results for the single unit cell will be discussed.

Although the total simulation time is only just over 2 ps, all of the hydronium ions visit multiple states, indicating the highly dynamic nature of the system. The number of clearly distinct minima explored varies between three and five, depending on which of the three cations are followed. Most importantly, all of the states that exist for long enough to undergo multiple vibrational oscillations are of the same form as the original model (i.e., two hydrogen bonds to hydroxyl groups and one to a sulfate anion), thus confirming that the first configuration is indeed broadly representative. Transitions between states by the hydroniums occur at different times and so there appears to be little, if any, correlation between the orientations of the cation sites. Combined with the rapid timescale for the reorientation, this observation further supports the highly disordered nature of the hydrogen positions associated with hydronium. This rapid reorientation of hydronium ions between many symmetry-equivalent preferred configurations is in line with the findings of Nielsen et al. (2007) from NMR data where they propose a complex motional averaging with rotation about multiple axes, but that falls short of isotropic motion.

The above dynamical simulations also give an indication of the reorientation mechanisms that occur; while the majority of transitions between states occur by rotation of the hydronium ion, at least one umbrella inversion was observed to take place. During some transitions a short-lived state would appear in which hydronium forms three hydrogen bonds to hydroxyl groups, though this configuration always rapidly reverts to a configuration of the original form.

One of the key questions pertaining to hydronium alunite is whether the H₃O⁺ and OH⁻ ions can really coexist in adjacent sites or whether neutralization will ultimately occur. In the course of the molecular dynamics, there are often moments in the simulation at which one of the O-H bonds of the hydronium becomes elongated while the hydrogen bond shortens toward a bonding distance. However, these are strictly vibrations and never persist long enough to execute a single oscillation as a distinct H₂O··HO state. Similarly, if a proton transfer is made between a hydronium cation and one of the atoms to which it is hydrogen bonded in a static calculation, followed by relaxation, the hydrogen atom migrates back to its original position.

In the present study, we have found no evidence for the neutralization of hydronium within the alunite structure; indeed, all of the results are consistent with this being a stable entity, at least

¹ Deposit item AM-10-031, cell parameters and coordinates. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

for the stoichiometric material. The connectivity of the alunite structure, in which the hydroxyl groups and sulfate anions are bonded to two and three aluminum cations, respectively, seems to be sufficient to stabilize the negatively charged components to the extent that protonation is disfavored. Contrary to a previous model for hydronium jarosite, we find that the H₃O⁺ ion is rotated away from the threefold axis passing through the A-cation site. This leads to a far greater number of degenerate orientations over which the hydronium ion can be disordered, and thereby lowers the associated hydrogen density at any region of space. Allowing for the further broadening of the hydrogen position due to nuclear quantum effects, this provides an explanation for why it has so far proved impossible to refine a partially occupied hydrogen site for the structure of these materials.

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