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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