

The existence and mobility of hydronium ion in the structure of jarosite

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Jarosite is a common mineral of acid mine drainage systems. The most common end-members are jarosite *s.s.* ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), natrojarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$), and hydronium jarosite ($(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$). Despite its ubiquitous presence as a component of the jarosite solid solution, the properties of hydronium jarosite are not known well. In particular, the question of the existence of the hydronium ion in this structure has not been resolved yet.

The structure of jarosite is built by triangular sheets of octahedra $\text{Fe}(\text{OH})_6$, decorated by sulfate tetrahedra. The Fe^{3+} sites are partially (5-15 %) vacant. The monovalent cations reside in cavities between the sheets.

We have investigated a series of jarosite samples and their deuterated analogs by ²H magic-angle spinning nuclear magnetic resonance (MAS NMR) and quasi-elastic neutron scattering (QENS) on ¹H atoms.

²H MAS NMR results clearly distinguish hydroxyls (OD) in the structure from scarce OD₂ groups bound to iron and abundant OD_n (*n* = 2 or 3) groups not bound to iron. The δ_{iso} values for these three sites are ≈ 0 , ≈ 70 , and ≈ 260 ppm, respectively. The OD₂ groups bound to iron correspond to water molecules that coordinate vacant sites in the structure. The OD_n groups are either OD₂ or OD₃ molecules in the cavities. Integration of the intensities of the peaks suggests that *n* = 3, i.e., the cavity is occupied by a D3O⁺ group. The shape of the NMR spectra indicates that the D3O⁺ deuterons are highly mobile and tumble in their cavities.

QENS spectra show that the hydrogen in the sample is in motion already at ~ 17 K. The quasi-elastic line is broadened when compared to the vanadium standard. The spectra collected at 50, 120, 170, 220, and 300 K show further broadening of the quasi-elastic line. Separation of the signal due to rotation and possible translation of the hydrogen atoms in the QENS spectra is now in progress.

Jarosites in acid mine drainage environments: Formation, mineralogy, stability

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Jarosites form a subgroup of the alunite supergroup of minerals, and have a general formula of $\text{AB}_3(\text{TO}_4)_2(\text{OH})_6$, where A represents cations with a coordination number greater than or equal to 9 (K^+ , Na^+ , NH_4^+ , H_3O^+ , Ag^+ , Tl^+ , Pb^{2+}), B represents cation sites with octahedral coordination (mainly Fe^{3+} , but also Cu^{2+}), and T represents cations with tetrahedral coordination (SO_4 , AsO_4) (Jambor 1999). Jarosites are commonly found in ferric-rich, acidic (pH < 3), oxic, acid mine drainage (AMD) environments, where they are important stores of SO_4 and of potentially toxic elements such as Pb and As.

In AMD environments such as the Río Tinto, Spain, and the Mathiatis mine, Cyprus, plumbojarosite [$\text{Pb}_{0.5}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$] and jarosite itself [$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$] are common, and form as a result of the decomposition of pyrite or precipitation of sulphate-rich, ferric solutions. Batch experiments and computational modelling, carried out to investigate the stability of jarosite, plumbojarosite and beudantite [$\text{PbFe}_3(\text{SO}_4)(\text{AsO}_4)(\text{OH})_6$] under acidic (pH 2) and alkaline (pH 8) conditions, have shown that these minerals all dissolve incongruently. The pH 2 dissolution of jarosite yields excess K and SO_4 relative to Fe in solution, which may be related to selective dissolution of the A- (K) and T- (SO_4) sites, since Fe is located deep within the T-O-T jarosite structure. Of the pH 2 dissolutions, only that of beudantite yields a secondary, Fe hydroxide-like phase.

The alkaline (pH 8) dissolutions all yield secondary phases: jarosite yields goethite, plumbojarosite and beudantite yield Fe hydroxide, and beudantite also yields PbSO_4 . There is evidence for some co-precipitation and resorption of the Pb and As in and onto the newly-formed phases, suggesting that the remainder of these potentially toxic elements may be released back to AMD waters.

Reference

Jambor, J. (1999) *Can. Miner.* **37**, 1323-1341.