Problematic

Jarosite s.s. – ideally KFe(OH)(SO4) – is a secondary iron sulphate very common in acid mine drainage (AMD) environments with high potassium content. This mineral is not only environmentally important because it may configure the ultimate mineral sink of lead and other hazardous metals (e.g. thallium), beyond silver, occurring frequently in the oxidized part of sulphide ore deposits, but it is also economically relevant within various hazardous metals environments with high potassium content. Therefore, the knowledge of its crystallographic and magnetic structures will be important, paradigmatic to other jarosite-like minerals.

Besides, the economical relevance within various hazardous metals environments with high potassium content. May configure the magnetic properties of this mineral, the jarosite crystal field stabilizes high spin-state ferrous ions, and this peculiar undistorted triangular motif - with fully occupied 3d-orbitals - allows an easy comparison and analysis of the electronic state of iron in these important sulphates.

Once many doubts still subsist concerning the exact crystal structure of Pb-rich and other jarosites, a comparative study on the electronic state of iron in these important sulphates was undertaken by comparing and analysing the pre-edge details of Fe 1s XANES spectra from various jarosites and structurally affine iron sulphates.

Experimental

X-ray absorption experiments were conducted at the ESRF using beam line ID-21 (9s) XANES and EXAFS spectra were collected in fluorescence yield (FY) mode with an energy-dispersive high-purity Ge-detector mounted perpendicular to the X-ray beam in the horizontal plane (fig.4) by irradiating a small area (1x1mm) of well crystallized mineral fragments.

A fixed-exit Si(220) monochromator assuring an energy resolution of 0.3 eV was used for the energy scans (7050-7350 eV). Metallic iron was used for energy calibration. Pre-edge details of XANES spectra were analysed using Fityk program (7) to deconvolute this spectral region into pseudo-Voigt components and assess iron electronic state.

Results and conclusions

The pre-edge features of Fe 1s XANES spectra collected from studied sulphate minerals are reproduced in fig.5. As expected (8), the average pre-peak centroid (fig.5a) clearly differentiates between ferro and ferric states: 7122.5 eV vs. 7114 eV, close to the published value of 1.4 eV for the energy difference (8). The similarity of the main pre-edge contributions is remarkable despite the occurrence of three distinct Fe2+ coordination environments in coquimbite comparatively to one unique situation in jarosite (table 1).

Conversely, the size and specification or electronic state of the large cation may explain the observed differences (fig.5a): (1) K+ and Na+ are closed shell, non-polarizable alkaline ions with different radius inducing a smaller ratio for non-lattoironic; (2) off-centering of Pb2+ ions within the icosahedron (fig.6a) which accommodates the lone-pair of 5s2 electrons from Pb2+ ions without symmetry breaking (fig.6b) a very special case of XANES spectra.

Crystallography of Jarosites

The jarosite-alunite mineral group has the simplified crystal chemical formula A1+n B2n+x (T1O1-x)2 (OH)6 (SO4)x (SiO4)1-x (Aic Bo3 (Tt O4)2 (OH)6). The jarosite-alunite group has the simplified crystal chemical formula A1+n B2n+x (T1O1-x)2 (OH)6 (SO4)x (SiO4)1-x (Aic Bo3 (Tt O4)2 (OH)6). In jarosite, the large cation is occupied by Ca2+ and Sr2+ ions, while in alunite by Pb2+ ions. The latter is able to accommodate the lone pair of 5s2 electrons from Pb2+ ions without symmetry breaking (fig.6b), owing to the presence of the lone pair of 5s2 electrons from Pb2+ ions without symmetry breaking (fig.6b), the presence of a larger cation in the structure.

References