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The atomic arrangement of ojuelaite, $\text{ZnFe}_2^{3+}(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$

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OJUELAITE was described from its occurrence at the Ojuela mine in Mapimi, Mexico by Cesbron *et al.* (1981). Those authors suggested that the phase was isostructural with whitmoreite (Moore *et al.*, 1974), a phase of interest because of the unique arrangement of Fe octahedra in its octahedral sheet. Cesbron *et al.* (1981) also suggested that ojuelaite was isostructural with arthurite, $\text{CuFe}_2^{3+}(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (Keller and Hess, 1978). The common fibrous habit of ojuelaite, however, has precluded structure determination.

We obtained a specimen of ojuelaite from the type locality that provided a single crystal suitable for structure determination. The structure study confirmed that ojuelaite is isostructural with whitmoreite and arthurite within the large constraints imposed by the requirements of the different substituent elements.

Experimental

Procedures for X-ray data collection and structure refinement are given in Ni *et al.* (1993); Table 1 lists details of data collection and structure refinement specific to this study. The atomic arrangement was refined using positional parameters of whitmoreite (Moore *et al.*, 1974) as starting parameters, although several atoms, particularly OW2, refined to positions with large deviations from the whitmoreite parameters.

The crystal was analysed using an electron microprobe (H_2O by difference) and yielded $(\text{Zn}_{0.77}\text{Fe}_{0.23})_{\Sigma 1.00} \text{Fe}_{2.00}(\text{AsO}_4)_{1.94}(\text{OH})_2 \cdot 3.75\text{H}_2\text{O}$ on the basis of $\text{Zn} + \text{Fe} = 3$. The presence of Fe in the Zn site is similar to the mixed composition of that

site in whitmoreite (Moore *et al.*, 1974). Refinement of electron occupancy of the site yielded 28.0 electrons, as opposed to 29.0 by electron probe, supporting the lack of saturation of the site by Zn. It is not known if the iron in the site is Fe^{2+} or if it is Fe^{3+} that is charge-balanced by a mechanism such as a concomitant $\text{O} \rightleftharpoons (\text{OH})$ substitution.

Table 2 lists atomic coordinates, equivalent isotropic thermal parameters, and bond valence sums before hydrogen bonding is calculated; Table 3 lists selected bond lengths. Structure factors and anisotropic thermal parameters may be obtained from the editor.

TABLE 1. Crystal data and results of ojuelaite structure refinement

| Cell Parameters ($P2_1/c$) | |
|--|-----------------------|
| $a(\text{\AA})$ | 10.237(1) |
| b | 9.662(3) |
| c | 5.562(1) |
| $\beta(^{\circ})$ | 94.36(1) |
| Theta Limits | 0 – 30° |
| Scan time (seconds) | ≤ 60 |
| Data collected | ± h , ± k , ± l |
| $R_{\text{merge}}(\%)$ | 1.8 |
| # Unique data | 1689 |
| # data > 5 σ_I | 1027 |
| $R(\%)$ | 2.4 |
| $R_w(\%)$ | 3.2 |
| Peaks on difference map ($e/\text{\AA}^3$), (+, –) | 0.88, 0.80 |

TABLE 2. Positional parameters, equivalent isotropic B, and bond valence sums (neglecting hydrogen bonding) for atoms in ojuelaite

| Atom | x | y | z | B (Å ²) | B.V.S. |
|------|------------|------------|------------|---------------------|--------|
| Zn | 0 | 0 | 0 | 0.72(1) | 1.98 |
| Fe | 0.45554(6) | 0.13639(7) | 0.3394(1) | 0.34(1) | 2.87 |
| As | 0.29680(4) | 0.42866(5) | 0.32682(8) | 0.346(6) | 4.90 |
| O1 | 0.3988(3) | 0.4860(4) | 0.1167(6) | 0.59(5) | 1.98 |
| O2 | 0.3561(3) | 0.4900(4) | 0.5989(6) | 0.63(6) | 1.67 |
| O3 | 0.1483(3) | 0.4926(4) | 0.2596(6) | 0.87(6) | 1.66 |
| O4 | 0.2962(3) | 0.2545(4) | 0.3186(6) | 0.66(5) | 1.76 |
| OH | 0.5414(3) | 0.2323(4) | 0.0782(6) | 0.61(5) | 1.04 |
| OW1 | 0.1299(3) | -0.0937(4) | 0.2916(6) | 1.34(7) | 0.25 |
| OW2 | 0.0456(4) | 0.1930(4) | 0.1277(7) | 1.46(7) | 0.40 |

Description of the structure

Moore *et al.* (1974) successfully solved and refined ($R = 0.14$) the whitmoreite atomic arrangement using film-derived intensities obtained from a twinned crystal. We base our description on their work, for it aptly extracts the salient features of the atomic arrangement of the mineral group that includes whitmoreite, arthurite, and ojuelaite.

The atomic arrangement of ojuelaite is based on a corrugated sheet of Fe octahedra that is unique among minerals. The sheet (Fig. 1) is formed of FeO₆ octahedra which share four vertices within the sheet. Two vertices (O1-O1) constitute a shared edge, and two others are corner-linked to adjacent octahedra by hydroxyl oxygens. The hydroxyls share adjacent vertices, and they are in *cis*-configuration relative to the octahedron.

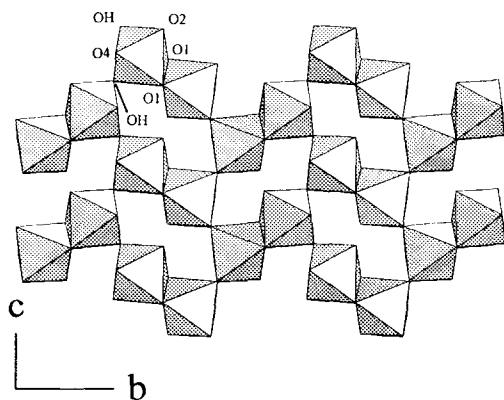


FIG. 1. Projection of ojuelaite iron octahedral sheet on (100).

TABLE 3. Selected bond distances in ojuelaite

| | | | |
|---------------|------------|---------|----------|
| Zn - O3 (× 2) | 2.099(3) Å | Fe - O1 | 2.083(3) |
| OW1 (× 2) | 2.212(4) | O1' | 2.062(3) |
| OW2 (× 2) | 2.037(4) | O2 | 2.027(3) |
| Mean | 2.116 | O4 | 1.988(3) |
| | | OH | 1.983(3) |
| As - O1 | 1.717(3) | OH' | 1.992(3) |
| O2 | 1.694(3) | Mean | 2.023 |
| O3 | 1.657(3) | | |
| O4 | 1.683(4) | | |
| Mean | 1.688 | | |

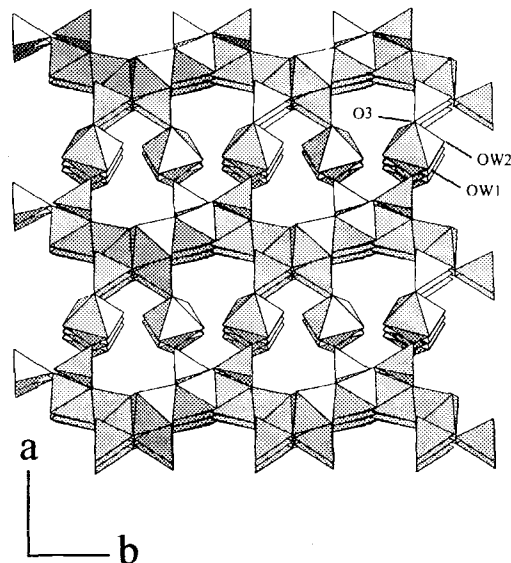


FIG. 2. Projection of ojuelaite structure on (001), illustrating linkage between iron octahedral sheets.

The corrugated sheets are linked ([001]) by AsO_4 tetrahedra and ZnO_6 octahedra (Fig. 2). The tetrahedra link to the Fe octahedral sheets, and tetrahedra from adjacent sheets share opposite corners of the ZnO_6 octahedra. The octahedra are surrounded by holes in the structure that provide sites for the water molecule hydrogen atoms.

The bonding of the ZnO_6 octahedron is of particular interest. Four of the octahedral ligands are water molecules ($2 \times \text{OW1}$, $2 \times \text{OW2}$), thus requiring extensive hydrogen bonding within the structure to alleviate over-bonding of the water oxygens. The bond valence sums in Table 2 support the conclusion that OW1 and OW2 are donors of hydrogen bonds, and O2, O3, and O4 are hydrogen bond receptors; O1 does not receive hydrogen bonds. This scheme of hydrogen bonding is similar to that deduced by (Moore *et al.*, 1974) in the isostructural phase whitmoreite. Attempts to locate the hydrogen atoms were not successful, typical of such a structure dominated by heavy ions.

KEYWORDS: ojuelaite, crystal structure, Mexico.

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