

MINERALOGICAL NOTES

THE CRYSTAL STRUCTURE AND THE CHEMICAL COMPOSITION OF VAUXITE

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The crystal structure of vauxite has been determined in the course of an investigation of the vauxite mineral group. In addition to vauxite two other minerals belong to this group: metavauxite $[\text{AlPO}_4\text{OH}(\text{OH})_2]_2[\text{Fe}^{2+}(\text{OH})_2]_6$ (Baur and Rama Rao, 1967), and paravauxite, $\text{Fe}^{2+}\text{Al}(\text{PO}_4)_2(\text{OH})_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ (Baur and Locy, to be published); paravauxite is isostructural with laueite (Moore, 1965). The crystal used for this study is from Llallagua, Bolivia. Three-dimensional X-ray data were collected on a precession camera with $\text{MoK}\alpha$ radiation. The crystals are, in agreement with Palache, Berman & Frondel (1951), triclinic with $a=9.13 \text{ \AA}$, $b=11.59 \text{ \AA}$, $c=6.14 \text{ \AA}$, $\alpha=98.3^\circ$, $\beta=92.0^\circ$, $\gamma=108.4^\circ$, $V=608 \text{ \AA}^3$, $Z=2$ and space group $P\bar{1}$. The structure was solved from a three-dimensional Patterson synthesis. At the present stage of refinement $R=0.108$ for 1900 observed F_{hkl} . The parameters describing the crystal structure are listed in Table 1. The main bond lengths are shown in Table 2, their estimated standard deviations are about 0.02 \AA .

The chemical composition of vauxite was given by Gordon (1944) as $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 7\text{H}_2\text{O}$. The calculated density using this composition is $D_x=2.51 \text{ g.cm}^{-3}$. This value does not compare very well with the density measured by Gordon (1944) $D_m=2.389 \text{ g.cm}^{-3}$. A new measurement of the density yielded $D_m=2.40 \text{ g.cm}^{-3}$ and thus confirmed Gordon's measured value. The calculated density can be brought into good agreement with the values of the measured density by assuming vauxite to be $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, since then $D_x=2.41 \text{ g.cm}^{-3}$. That this is the correct composition was proved by the structure determination: only sixteen oxygen atom positions could be located. A difference electron density map based on all available F_{hkl} failed to show any electron density which could be interpreted as an additional, seventeenth oxygen atom position.

The structure is characterized by infinite chains of coordination octahedra which extend parallel to $[001]$ (see Fig. 1). The central cations of these octahedra are alternately $\text{Fe}(2)$ and $\text{Al}(2)$; The octahedra in these chains share the edge $\text{O}(p5)\text{-O}(h10)$. Parallel to this octahedral chain, and flanking it on two opposite sides, are vertex-linked chains consisting of phosphate tetrahedra around $P(2)$ alternating with coordination octahedra around $\text{Al}(1)$. The mixed tetrahedral-octahedral chains are linked through vertices $\text{O}(p5)$ and $\text{O}(h10)$ to the octahedral chain. This triple

TABLE 1. VAUXITE, POSITIONAL AND THERMAL PARAMETERS.
 x, y, z IN FRACTIONS OF THE CELL EDGE, B IN Å²

Atom	x	y	z	B
Fe(1)	0.000	0.000	0.000	1.1
Fe(2)	0.000	0.500	0.000	0.6
Al(1)	0.667	0.291	0.187	0.6
Al(2)	0.000	0.500	0.500	0.5
Al(3)	0.500	0.500	0.000	0.5
P(1)	0.990	0.264	0.215	0.7
P(2)	0.310	0.639	0.291	0.5
O(p1)	0.812	0.208	0.202	0.8
O(p2)	0.035	0.329	0.015	0.9
O(p3)	0.046	0.353	0.429	0.8
O(p4)	0.063	0.160	0.211	1.2
O(p5)	0.137	0.571	0.296	0.6
O(p6)	0.625	0.285	0.483	0.7
O(p7)	0.329	0.725	0.121	0.8
O(p8)	0.396	0.546	0.228	0.8
O(h9)	0.532	0.384	0.165	0.9
O(h10)	0.838	0.448	0.258	0.7
O(w11)	0.768	0.961	0.142	1.5
O(w12)	0.058	0.907	0.276	2.7
O(w13)	0.502	0.136	0.120	1.0
O(w14)	0.694	0.620	0.143	1.1
O(w15)	0.380	0.958	0.341	1.9
O(w16)	0.706	0.808	0.468	1.5

chain is further interlinked by the phosphate tetrahedron around $P(1)$, which shares vertices with the octahedra around $Al(1)$, $Al(2)$ and $Fe(2)$. This infinite triple chain unit $[FeAl_3(PO_4)_4(OH)_4(OH_2)_2]^{5-}$ is connected to neighboring units of the same kind via vertex-linked $Al(3)$ coordination octahedra in direction $[100]$, and via $Fe(1)$ coordination octahedra in direction $[010]$.

Two of the water oxygen atoms are not coordinated to any cations, but are situated in channels which extend parallel $[001]$ through the structure. These water molecules are hydrogen bonded to the framework structure. Hydrogen bonds are indicated in Table 2 by arrows pointing to the acceptor atom of the bond. The distance $O(w15)-O(p6)$ is too long to be accepted as a hydrogen bond without further proof. Therefore, this assignment is only tentative. The hydroxyl oxygen atom $O(h9)$ does not form a hydrogen bond: its next neighbors in a direction in which a hydrogen bond might be formed are at a distance of 3.7 Å.

The ratio of cations (Fe, Al, and P) to oxygen atoms coordinated to them is in vauxite 5:14, in paravauxite 5:16, and in metavauxite 5:18.

TABLE 2. BOND LENGTHS IN VAUXITE

Fe(1)-O(p4)	2.01 Å	Al(2)-O(p3)	1.87 Å
Fe(1)-O(w11)	2.26 Å	Al(2)-O(p5)	1.89 Å
Fe(1)-O(w12)	2.26 Å	Al(2)-O(h10)	1.95 Å
Fe(2)-O(p2)	2.12 Å	Al(3)-O(p8)	1.83 Å
Fe(2)-O(p5)	2.08 Å	Al(3)-O(h9)	1.88 Å
Fe(2)-O(h10)	2.22 Å	Al(3)-O(w14)	1.95 Å
P(1)-O(p1)	1.54 Å	O(h10)→O(w14)	2.86 Å
P(1)-O(p2)	1.54 Å	O(w11)→O(p1)	2.73 Å
P(1)-O(p3)	1.52 Å	O(w11)→O(w16)	2.82 Å
P(1)-O(p4)	1.54 Å	O(w12)→O(p2)	2.91 Å
P(2)-O(p5)	1.53 Å	O(w12)→O(w15)	2.82 Å
P(2)-O(p6)	1.52 Å	O(w13)→O(w11)	2.72 Å
P(2)-O(p7)	1.52 Å	O(w13)→O(w15)	2.60 Å
P(2)-O(p8)	1.53 Å	O(w14)→O(p2)	2.61 Å
Al(1)-O(p1)	1.88 Å	O(w14)→O(w16)	2.71 Å
Al(1)-O(p6)	1.88 Å	O(w15)→O(p7)	2.73 Å
Al(1)-O(p7)	1.88 Å	O(w15)→O(p6)	3.16 Å
Al(1)-O(h9)	1.89 Å	O(w16)→O(p4)	2.74 Å
Al(1)-O(h10)	1.97 Å	O(w16)→O(p6)	2.92 Å
Al(1)-O(w13)	1.92 Å		

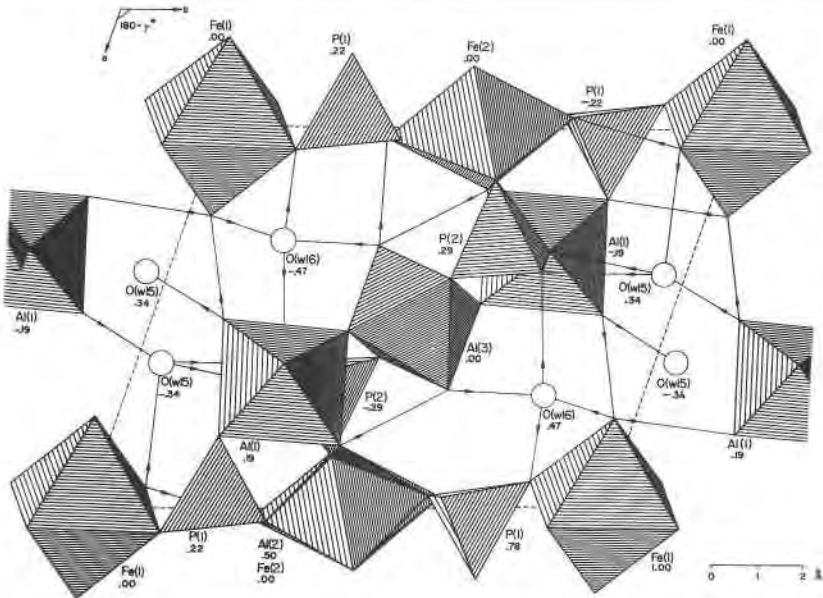


FIG. 1. Vauxite, view [001]. In order to make the presentation clearer part of the coordination polyhedra and some of the hydrogen bonds have been left out. Water molecules, which are not bonded to cations are represented by circles. Hydrogen bonds are indicated by arrows pointing towards acceptor atoms of the bonds.

This shows that the degree of linkage of the coordination polyhedra is highest in vauxite, lowest in metavauxite. There is no similarity between the crystal structure of vauxite and the structures of the other two minerals of the vauxite group. This is interesting in view of the fact that all three minerals occur together as secondary minerals.

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ELECTRON DIFFRACTION DATA FOR SOME MEMBERS OF THE METATORBERNITE GROUP

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INTRODUCTION

The metatorbernite group of minerals is characterized by the formula $A^z(\text{UO}_2\text{XO}_4)_z \cdot n\text{H}_2\text{O}$, where A may be almost any monovalent or divalent cation, and X may be P or As. These minerals have received a great deal of study, but there are still problems concerning the crystallography of some members of the group. Different authors arrive at different results in the determination of unit cell and space group (Alver and Sellevol, 1957; Donnay and Donnay, 1955; Nuffield and Milne, 1953; Ross, 1963; Ross, Evans and Appleman, 1964; Ross and Evans, 1965; Takano, 1961; Volborth, 1959).

Up to 1955 a tetragonal cell with $a = 6.9 \text{ \AA}$ was assigned to the minerals of the group. Weak reflections showing that, for some members of the group, the cell with $a = 6.9 \text{ \AA}$ was a pseudo cell were observed later by different authors. Donnay (1955) for instance, using the integrating precession technique, found for uranocircite a tetragonal cell with $a = 9.87 \text{ \AA}$.

To our knowledge, published data have been obtained exclusively by