

Refinement of the Crystal Structure of Fornacite Using the Rietveld Method

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Abstract—The crystal structure of fornacite $\text{Pb}_2(\text{Cu,Fe})[\text{CrO}_4(\text{As,P})\text{O}_4\text{OH}]$ from the Berezovskii deposit (Central Urals, Russia) was refined by X-ray powder diffraction data using the Rietveld method. Fornacite is monoclinic, space group $P2_1/c$, the unit cell dimensions are $a = 8.09015(12)$, $b = 5.90913(9)$, $c = 17.4839(2)$ Å, $\beta = 109.99(2)^\circ$, $V = 785.5(3)$ Å³, and $Z = 4$. The structure was refined in the isotropic approximation of the atomic displacement parameters up to $R_p = 0.0516$, $R_{wp} = 0.0692$, $R_B = 0.0229$, and $R_F = 0.0200$. The fornacite structure is similar to that of minerals of the brackebuschite-group and consists of heteropolyhedral chains, built by the columns of edge-sharing Cu^{2+}O_6 octahedra connected with isolated Cr^{6+}O_4 and As^{5+}O_4 tetrahedra. The chains are linked by ninefold Pb^{2+} polyhedra.

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Fornacite, which was described for the first time in Djoué (Congo) in 1915 [1], is a monoclinic Cu–Pb chromate–arsenate with the formula $\text{Pb}_2(\text{Cu,Fe})[\text{CrO}_4(\text{As,P})\text{O}_4\text{OH}]$ [2–4]. The authors of [4] identified its unit cell dimensions and stoichiometry and suggested that it is isostructural with vauquelinite $\text{Pb}_2\text{Cu}(\text{CrO}_4)(\text{PO})_4(\text{OH})$ [5, 6]. In 1967, the structure of a fornacite single-crystal from the Renéville Mine (Congo) was solved: space group $P2_1/c$, $a = 8.101(7)$ Å, $b = 5.893(11)$ Å, $c = 17.547(9)$ Å, $\beta = 110.00(3)^\circ$, $Z = 4$ ($R_{hkl} = 0.098$) [7]. The structural relationship of vauquelinite, fornacite, tsumebite $\text{Pb}_2\text{Cu}(\text{SO}_4)(\text{PO})_4(\text{OH})$, and brackebuschite $\text{Pb}_2(\text{Mn,Fe})(\text{VO}_4)_2 \cdot \text{H}_2\text{O}$ was reported at the same time [8], although the two latter minerals are characterized by different space groups and are significantly distinct in the unit cell dimensions.

In 1995, fornacite was found for the first time in Russia in a supergene zone of the Berezovskii gold deposit in the Central Urals [9]. As was shown by our recent studies, it is widespread in the famous crocoite occurrence at Mt. Uspenskaya in the northern part of the deposit. Aggregates of fornacite occur in the oxidation products of the pyrite–galena–fahlore pockets in quartz veins among listvenites at a depth of about 15 m. Fornacite frequently contains phosphorous, being transitional to vauquelinite, and mostly occurs in cavities of oxide–arsenate pseudomorphoses after fahlore or incrusts in the walls of cavities of dissolution of sulfides and carbonates in veined quartz in the immediate vicinity of these pseudomorphoses. It is closely associated with mimetite, minerals of the beudantite–segnite

series, bayldonite, duftite, gartrellite, crocoite, As-bearing vauquelinite, bindheimite, goethite, and other minerals. Fornacite forms druses, crusts, and radial aggregates of dark green, brownish yellow, or dark brown to black (with all intermediate colors) wedge-shaped, platy or spear-like (almost acicular) crystals up to 0.5 cm in size. They are always more-or-less split, which hampers single-crystal X-ray study. Thus, a complete XRD analysis using the Rietveld method chosen to refine the mineral structure allowed us to achieve a lower divergence factor relative to the Congo fornacite single crystal [7].

Coordinates and isotropic displacement parameters (Å²) of atoms in the fornacite structure

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Pb(1)	0.2175(1)	0.2272(1)	0.3748(5)	2.28(13)
Pb(2)	0.2237(5)	0.7689(2)	0.0594(3)	2.09(12)
Cu	0.4887(4)	0.5023(9)	0.2485(9)	1.6(3)
As _{0.79(2)} P _{0.21(3)}	0.4854(3)	0.2361(2)	0.0798(9)	0.7(4)
Cr	0.0486(3)	0.2603(4)	0.1583(9)	1.9(4)
O(1)	0.5414(9)	0.0141(9)	0.1472(1)	1.5(9)
O(2)	0.4674(2)	0.4920(5)	0.1394(9)	2.5(9)
O(3)	0.2953(2)	0.2076(5)	0.0150(1)	2.9(9)
O(4)	0.6422(6)	0.2985(6)	0.0446(6)	2.7(9)
O(5)	0.9935(7)	0.0306(1)	0.1004(3)	1.1(9)
O(6)	−0.0073(7)	0.4784(8)	0.0941(7)	3.0(9)
O(7)	0.2537(4)	0.2493(2)	0.2206(1)	2.6(9)
O(8)	0.9372(5)	0.2673(8)	0.2228(1)	2.3(9)
O(9)	0.3451(4)	0.7692(3)	0.2136(3)	1.9(9)

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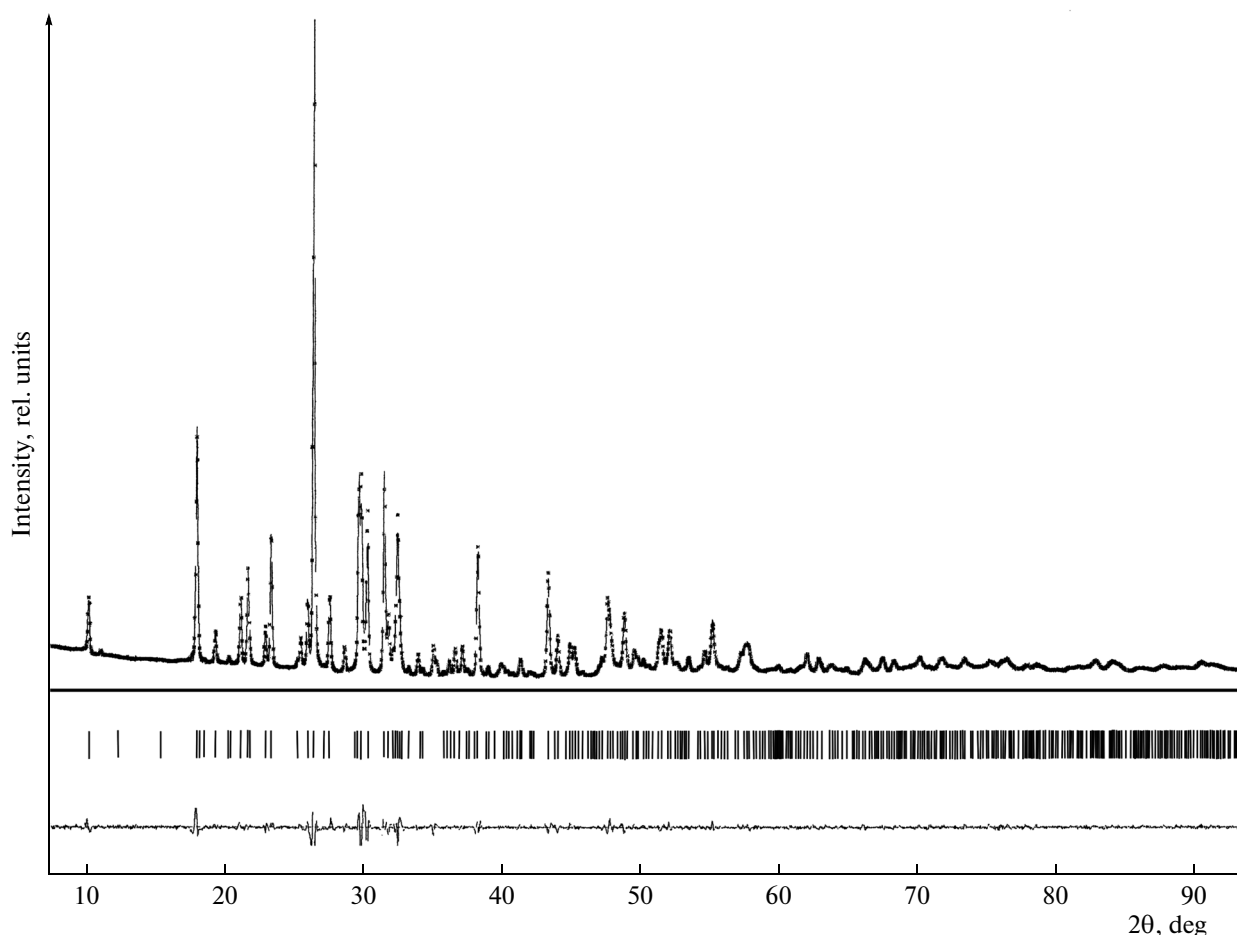


Fig. 1. Theoretical (stars) and experimental (solid line) X-ray patterns of fornacite.

The chemical composition of fornacite from the Berezovskii deposit widely varies: $\text{Pb}_{1.95-2.03}\text{Ca}_{0.00-0.01}\text{Cu}_{0.92-1.05}\text{Cr}_{0.90-1.05}\text{As}_{0.67-0.92}\text{P}_{0.03-0.28}\text{O}_8(\text{OH})$. It is close to the simplified formula $\text{Pb}_2\text{Cu}(\text{CrO}_4)[(\text{As},\text{P})\text{O}_4](\text{OH})$ with a quite variable As/P ratio, which is locally distinct more than twice in adjacent crystals.

The X-ray powder pattern of fornacite was obtained using the Debye–Scherrer scheme on a STOE-STADI MP powder diffractometer with a curved Ge(111) monochromator, which provides monochromatic $\text{CuK}\alpha_1$ -radiation ($\lambda = 1.54056 \text{ \AA}$). The data were collected at room temperature in a step-by-step overlapping of scanning areas using a position-sensitive linear detector with a catch angle of 5° along 2θ and a channel width of 0.02° in the range of $8.00^\circ < 2\theta < 93.38^\circ$. The powder sample was placed in a glass capillary ($d = 0.5 \text{ mm}$), which was mounted on a rotating goniometric head.

The experimental data were processed, and the crystal structure of fornacite was refined using the WinX^{Pow} [10] and WYRIET 3.3 [11] programs. The structure of fornacite from [7] was accepted as the ini-

tial model. The Pearson-VII function was used for peak profiles modeling. The crystal structure of fornacite was refined with a step-by-step addition of the refined parameters with constant graphical background modeling. The final values of the divergence factors are $R_p = 0.0516$, $R_{wp} = 0.0692$, $R_{\text{Bragg}} = 0.0229$, and $R_F = 0.0200$. The Durbin–Watson statistics (*DWD*) is 0.76 [12]. At the final stage of refinement, the unit cell dimensions were $a = 8.09015(12) \text{ \AA}$, $b = 5.90913(9) \text{ \AA}$, $c = 17.4839(2) \text{ \AA}$, $\beta = 109.99(2)^\circ$, $V = 785.5(3) \text{ \AA}^3$, and $Z = 4$. The coordinates and isotropic displacement parameters of atoms are given in Table 1. The experimental and calculated X-ray patterns and fornacite structure are shown in Figs. 1 and 2, respectively.

Our study confirmed the fornacite structure suggested in [7]. As was shown in [6], this mineral and its phosphorous analogue (vauquelinite) are structurally related to the minerals of the brackebuschite group. Similarly to them and structurally close minerals, fornacite should be related to the Cu-bearing oxysalts, the major structural element of which is the endless polyhedral chains of octahedrally (*M*) and tetrahe-

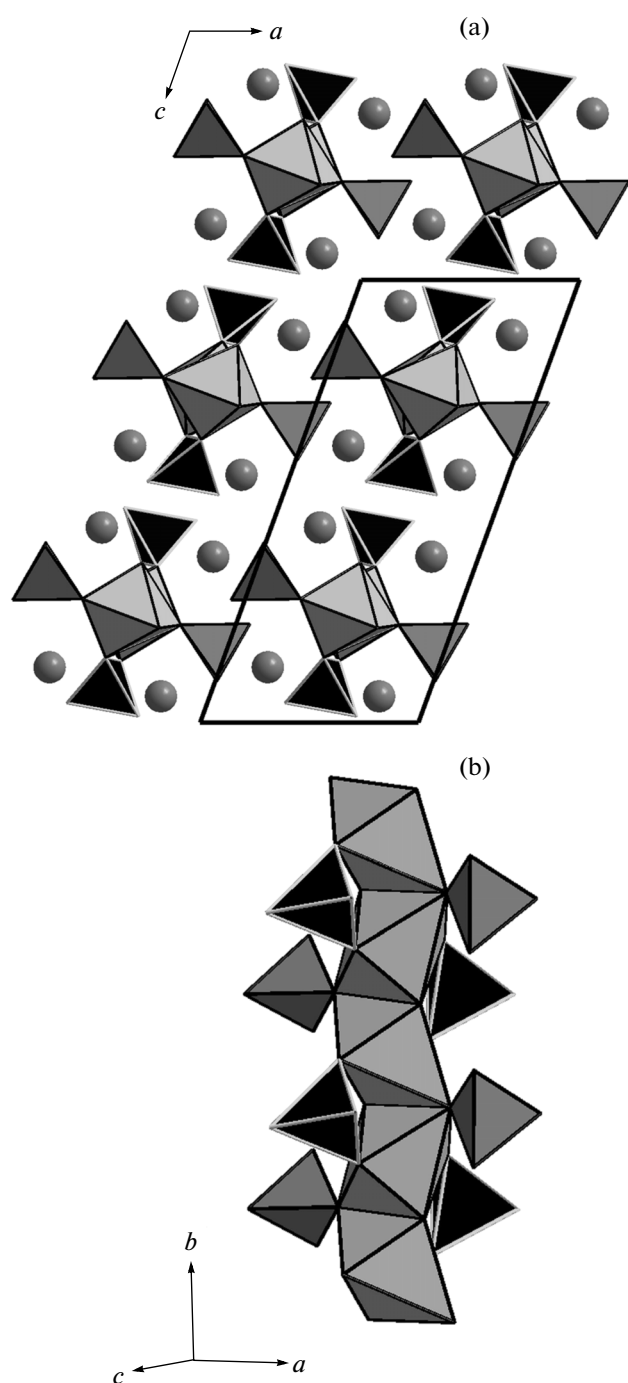


Fig. 2. Crystal structure of fornacite in *ac* projection (a), heteropolyhedral chain of CuO_6 octahedra (gray) and $(\text{As,P})\text{O}_4$ (black) and CrO_4 (dark gray) tetrahedra (b). Gray spheres are the positions of the Pb cations.

drally (*T*) coordinated cations [13]. The representatives of this group, in turn, are subdivided depending on the type of the polyhedral linkage inside the chain. Fornacite contains *M–M–T* chains (*M–M* is the linkage of MO_6 octahedra through the common edges and

M–T is the linkage of tetrahedra and octahedra via common vertices). The major structural unit of the mixed chains in fornacite is a column, which is formed by Cu^{2+} -centered octahedra sharing edges and tetrahedra centered by Cr^{6+} (the average Cr–O distance is 1.66 Å) and by As^{5+} (with impurity of P) (average $(\text{As,P})\text{–O}$ distance is 1.70 Å) (Fig. 2b). The Cu^{2+} -centered octahedra are characterized by the Jahn–Teller distortion with four Cu–O distances of 1.86(9)–1.93(7) Å and another two elongated (2.34(7) and 2.45(7) Å) distances. The role of the CrO_4 and $(\text{As,P})\text{O}_4$ tetrahedra is distinct: the latter reinforces the contacts between the adjacent Cu octahedra, linking with them by two vertices, whereas the first one has only one common vertex with the Cu octahedra. The heteropolyhedral chains in the fornacite structure are elongated along the *b* axis and are connected by the ninefold Pb^{2+} centered polyhedra located in two independent crystallographic positions. The interatomic Pb–O distances in these polyhedra are 2.34(4)–3.22(5) and 2.45(4)–3.03(4) Å, respectively.

The chains composed of the Al-centered octahedra and CO_3 triangles, which were described in the structure of dundasite $\text{PbAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$ [14], are geometrically similar to the mixed octahedral–tetrahedral chains in fornacite. The arrangement of CO_3 groups in dundasite and the $(\text{As,P})\text{O}_4$ tetrahedra in fornacite is similar: each CO_3 triangle in dundasite is linked with a column of Al octahedra by two common vertices. The topological similarity of the major structural elements of the brackebuschite-group minerals, structurally close compounds (including fornacite), and carbonates of the dundasite family (dundasite, dresserite, strontiodresserite, petterdite) causes the close unit cell dimensions along which heteropolyhedral chains are elongated: $b = 5.91$ Å in fornacite and $c = 5.62$ Å in dundasite. The mineralogical and genetic crystal chemistry of petterdite $\text{PbCr}_2(\text{CO}_3)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$, that is an analog of dundasite with Cr^{3+} instead of Al [15], is also interesting. It is formed in the same objects as minerals of the vauquelinite–fornacite series but at the earlier supergene stages, when the portion of Cr has not yet been oxidized to Cr^{6+} . A couple of topologically related Pb oxysalts (petterdite–fornacite/vauquelinite) is a striking example of the sharp change in the structural role of Cr during the variation in its valence. Cr^{3+} in petterdite implements the same cation function as Cu^{2+} in fornacite, forming the chain octahedral motive in contrast to the typical anion-forming Cr^{6+} : the isolated tetrahedral CrO_4^{2-} anions occupy the same position in the structure as the triangle CO_3^{2-} in petterdite.

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