

TURANITE, $\text{Cu}^{2+}_5(\text{V}^{5+}\text{O}_4)_2(\text{OH})_4$, FROM THE TYUYA–MUYUN RADIUM–URANIUM DEPOSIT, OSH DISTRICT, KYRGYZSTAN: A NEW STRUCTURE FOR AN OLD MINERAL

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ABSTRACT

The crystal structure of turanite, $\text{Cu}^{2+}_5(\text{V}^{5+}\text{O}_4)_2(\text{OH})_4$, from the Tyuya–Muyun Ra–U deposit, the Alai Ridge foothills, Osh district, Kyrgyzstan, triclinic, space group $P\bar{1}$, a 5.3834(2), b 6.2736(3), c 6.8454(3) Å, α 86.169(1), β 91.681(1), γ 92.425(1)°, V 230.38(2) Å³, $Z = 1$, has been solved by direct methods and refined to an R index of 2.2% based on 1332 observed [$F_o > 4\sigma F$] unique reflections measured with $\text{MoK}\alpha$ X-radiation and a Bruker $P4$ diffractometer equipped with a CCD detector. Chemical analysis by electron microprobe gave CuO 62.94, V₂O₅ 28.90, H₂O 5.85, sum 97.69 wt.%; the amount of H₂O was determined by crystal-structure analysis. The resulting empirical formula on the basis of 12 anions (including OH = 4 *apfu*) is $\text{Cu}^{2+}_{4.97}(\text{V}^{5+}\text{O}_4)_2(\text{OH})_{4.08}$. There are three distinct Cu sites fully occupied by Cu²⁺ and octahedrally coordinated by four O atoms and two (OH) groups, with $\langle \text{Cu–O, OH} \rangle = 2.115$ Å. The (Cuφ₆) octahedra (φ = O, OH) form a sheet of edge-sharing octahedra (with vacancies, oct : vac = 5 : 1) parallel to (011). On each side of the vacant octahedron, a (VO₄) tetrahedron is attached to three anions of the sheet and points away from the sheet to be attached to an anion of the adjacent sheet. Thus the (Cuφ₆) octahedra and (VO₄) tetrahedra constitute a framework, within which the sheets are also linked by hydrogen bonding from (OH) groups of one sheet to O anions of adjacent sheets. Turanite can be considered as a framework structure with interrupted sheets of (Cuφ₆) octahedra decorated by (VO₄) tetrahedra, and is related to the structures of cornubite, ciangiullite, gordaite, bechererite, chalcophyllite, ramsbeckite and simonkolleite.

Keywords: turanite, crystal structure, Tyuya–Muyun, Osh district, Kyrgyzstan.

SOMMAIRE

Nous avons résolu la structure cristalline de la turanite, $\text{Cu}^{2+}_5(\text{V}^{5+}\text{O}_4)_2(\text{OH})_4$, provenant de la localité type, le gisement de Ra–U de Tyuya–Muyun, crêtes d’Alaï, district de Osh, au Kirgizstan, triclinique, groupe spatial $P\bar{1}$, a 5.3834(2), b 6.2736(3), c 6.8454(3) Å, α 86.169(1), β 91.681(1), γ 92.425(1)°, V 230.38(2) Å³, $Z = 1$, par méthodes directes, et nous l’avons affiné jusqu’à un résidu R de 2.2% en utilisant 1332 réflexions uniques observées [$F_o > 4\sigma F$] avec rayonnement $\text{MoK}\alpha$ et un diffractomètre Bruker $P4$ muni d’un détecteur CCD. Une analyse chimique avec une microsonde électronique a donné CuO 62.94, V₂O₅ 28.90, H₂O 5.85, somme 97.69% (poids); la teneur en H₂O a été établie par analyse de la structure. La formule empirique suivante est calculée sur une base de 12 anions (y inclus quatre groupes OH par unité formulaire): $\text{Cu}^{2+}_{4.97}(\text{V}^{5+}\text{O}_4)_2(\text{OH})_{4.08}$. Il y a trois sites Cu distincts, qu’occupe le Cu²⁺ en coordinence octaédrique, entouré de quatre atomes O et deux groupes (OH), avec $\langle \text{Cu–O, OH} \rangle = 2.115$ Å. Les agencements (Cuφ₆) (φ: O, OH) forment un feuillet d’octaèdres à arêtes partagées, parallèle à (011), dans lequel le rapport octaèdres à lacunes est 5 : 1. De chaque côté de l’octaèdre vacant, un tétraèdre (VO₄) se rattache aux trois anions du feuillet et pointe dans la direction opposée, pour ainsi se rattacher au feuillet adjacent. Les octaèdres (Cuφ₆) et les tétraèdres (VO₄) constituent ainsi une trame, dans laquelle les feuillets sont aussi interliés par liaisons hydrogène venant des groupes OH d’un feuillet, et dirigés vers les anions O d’un feuillet adjacent. La turanite serait donc une structure en trame ayant des feuillets interrompus d’octaèdres (Cuφ₆) décorés par des tétraèdres (VO₄), avec des points de ressemblance à la structure de la cornubite, la ciangiullite, la gordaïte, la bechererite, la chalcophyllite, la ramsbeckite et la simonkolléite.

(Traduit par la Rédaction)

Mots-clés: turanite, structure cristalline, Tyuya–Muyun, district de Osh, Kirgizstan.

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INTRODUCTION

Turanite, $\text{Cu}_5(\text{VO}_4)_2(\text{OH})_4$, was described as a new mineral from the Tyuya–Muyun radium–uranium deposit, in the foothills of the Alai range, Osh district, Kyrgyzstan (the former Fergana district) by Nenadkevich (1909). The name turanite is in reference to the locality, which occurs at “the southern frontier of the Turan basin” (Nenadkevich 1909). The mineralogy of the Tyuya–Muyun deposit has been thoroughly investigated by several authors (Alexandrov 1923, Fersman 1928, Suloev & Ponomarev 1934, Smol’yaninova 1970). Kazansky (1970) summarized the geological and structural characteristics of the Tyuya–Muyun deposit. It occurs in intensely deformed Carboniferous carbonate rocks; the country rocks are synclinally folded with traversing faults. The carbonate rocks show tectonic fissures and disjunctive joints, and the morphology of the orebodies is related to the karst topography. The ore-bearing marbles, with associated quartz–barite mineralization, contain tyuyamunite, $\text{Ca}(\text{U}^{4+}\text{O}_2)_2\text{V}^{4+}_2\text{O}_8(\text{H}_2\text{O})_{5-8}$, tangeite, $\text{CaCu}^{2+}(\text{V}^{5+}\text{O}_4)(\text{OH})$, malachite, $\text{Cu}^{2+}_2(\text{CO}_3)(\text{OH})_2$, chrysocolla, $(\text{Cu}^{2+},\text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{H}_2\text{O})_n$, and turanite. Smol’yaninova (1970) reported two additional vanadates, descloizite, $\text{Pb}^{2+}_2\text{Zn}(\text{VO}_4)(\text{OH})$, and vanadinite, $\text{Pb}^{2+}_5(\text{V}^{5+}\text{O}_4)\text{Cl}$.

Turanite has long been recognized as an incompletely described mineral species, but it has recently been reported from the Van-Nav-San claim, Gibellini district, Nevada, and the Gold Quarry mine, Maggie Creek district, Nevada (Pullman & Thomsson 1999,

Castor & Ferdock 2004). The work presented here confirms turanite as a valid mineral species.

SAMPLE

For the single-crystal X-ray study, we used two grains from specimen MM No. 3578 in the systematic collection of the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia. The specimen was taken from the Tyuya–Muyun deposit by K.A. Nenadkevich in 1910 and deposited at the Museum in 1912. Therefore, this material is the holotype specimen. Turanite consists of spherulitic radial aggregates filling a 2×3 cm cavity in barite (Fig. 1). The mineral is deep olive-green in color, similar to volborthite, and is easily distinguished from malachite and acicular light-green crystals of tangeite (<0.2 mm) on the surface of the spherulites of turanite, which attain 6 mm in diameter. Under the optical microscope, all turanite crystals show polysynthetic twinning and a tabular habit. It is difficult to see any habit for turanite crystals in the specimen MM No. 3578 because of a crust of tangeite crystals. However, the tabular habit of turanite is easily seen in the SEM image of a crystal collected recently in the Tyuya–Muyun deposit (Fig. 2).

CHEMICAL ANALYSIS

Chemical analyses (Table 1) were done with a JXA-50A electron microprobe operating at 20 kV and 20 nA. The following standards and crystals were used for K or



FIG. 1. The holotype specimen of turanite (#3578) from the collection of the Fersman Mineralogical Museum (Moscow, Russia). Size of sample is 4.5×7.5 cm. Photograph by N.A. Pekova.

L X-ray lines: Cu: diopside $\text{CuSiO}_2(\text{OH})_2$; V: metallic; (H_2O) was calculated from structure solution and refinement. Data were reduced using the $\phi(\rho Z)$ procedure of Pouchou & Pichoir (1985). The chemical composition of turanite is given in Table 1 and is the mean of four determinations. The unit formula was calculated on the basis of twelve anions, 8 O atoms + 4 (OH) groups. The empirical formula, $\text{Cu}^{2+}_{4.97}(\text{V}^{5+}\text{O}_4)_{2.0}(\text{OH})_{4.08}$, is very close to the ideal composition, $\text{Cu}^{2+}_5(\text{V}^{5+}\text{O}_4)_2(\text{OH})_4$.

X-RAY DATA COLLECTION AND STRUCTURE SOLUTION

A small crystal measuring $20 \times 50 \times 60 \mu\text{m}$ was cut from a multi-twinned turanite intergrowth, attached to a glass fiber and mounted on a Bruker *P4* automated four-circle diffractometer equipped with APEX 4K CCD detector and $\text{MoK}\alpha$ X-radiation. The intensities of 9428 reflections with $\bar{7} < h < 7$, $\bar{8} < k < 8$, $\bar{9} < l < 9$ were collected to $59.93^\circ 2\theta$ using 45 s per 0.2° frame, and an empirical absorption-correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters (Table 2) were obtained from 4578 reflections with $I > 10\sigma I$. The crystal structure of turanite was solved by direct methods and refined to an *R* index of 2.2% for 1332 independent observed reflections with the SHELXTL 5.1 system of programs (Sheldrick 1997). Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). Site occupancies were refined for three *Cu* sites and one *V* site to confirm that they are solely occupied by these particular atoms. In the last stages of the refinement, two H atoms of two (OH) groups were found in the difference-Fourier map and included in the refinement with two types of constraints: (1) the distances O(donor)–H were softly fixed at 0.98 Å, and (2) the isotropic-displacement factor for a H atom was constrained to be 1.5 times larger than the displacement parameter of the O atom of the associated (OH) group. Final atom coordinates and displacement parameters are given in Table 3, selected interatomic distances are listed in Table 4, Table 5 contains hydrogen bonding information, Table 6 gives the bond valences, and Table 7 lists related minerals. Observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 1. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*) FOR TURANITE

| | | | |
|------------------------|-------|------------------|------|
| CuO | 62.94 | Cu^{2+} | 4.97 |
| V_2O_5 | 28.90 | V^{5+} | 2.00 |
| H_2O^* | 5.85 | H^+ | 4.08 |
| Total | 97.69 | | |

* calculated from structure refinement

DESCRIPTION OF THE STRUCTURE

Coordination of the cations

There are three unique *Cu* sites in turanite, each octahedrally coordinated and fully occupied by Cu (Figs. 3a, b). The *Cu*(1) site is coordinated by four (OH) groups and two O atoms, with a $\langle \text{Cu}-(\text{OH}), \text{O} \rangle$ distance of 2.114 Å. The *Cu*(2) and *Cu*(3) sites are each coordinated by four O atoms and two (OH) groups, with a

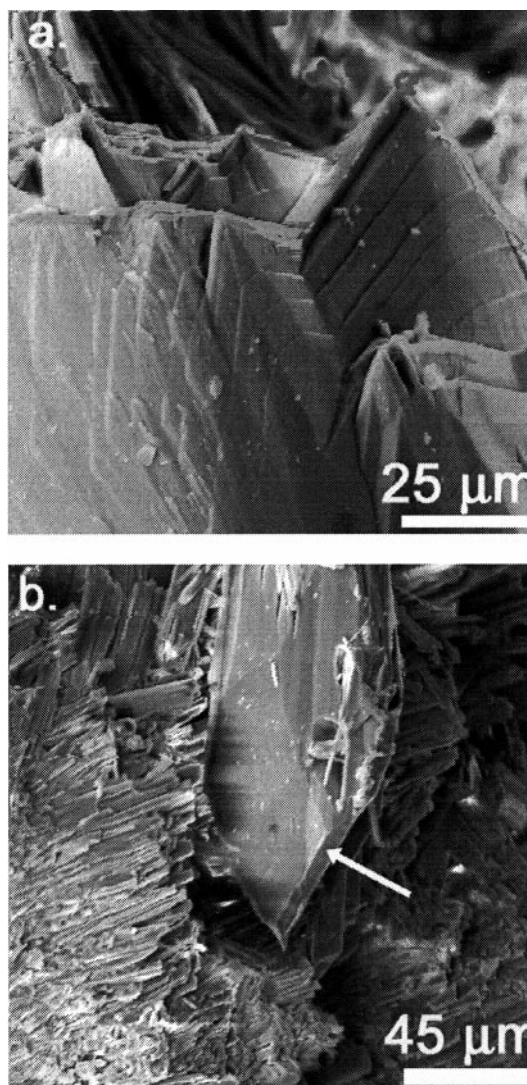


Fig. 2. SEM image of turanite crystals: (a) parallel intergrown crystals; (b) a tabular crystal (shown by arrow) among small crystals of tangeite.

$\langle \text{Cu}(2,3)\text{-O}(\text{OH}) \rangle$ distance of 2.116 Å. Each $(\text{Cu}^{2+}\phi_6)$ octahedron has four short equatorial bonds and two long apical bonds (Fig. 3b, Table 4), in accord with Burns & Hawthorne (1995, 1996), who showed that octahedrally coordinated Cu^{2+} is characterized by elongation (rather than shortening) of apical bonds. The directions of elon-

gation for the $\text{Cu}(1)$ and $\text{Cu}(2)$ octahedra are orthogonal to $[01\bar{1}]$, whereas for the $\text{Cu}(3)$ octahedron, it is oblique to $[01\bar{1}]$. This is a result of the bond-valence requirements of the coordinating O atoms and (OH) groups and the connectivity of polyhedra in the structure. The $\text{Cu}(1)$ and $\text{Cu}(2)$ octahedra share common edges to form a chain along $[01\bar{1}]$ with a repeat sequence $[\text{Cu}(1) = \text{Cu}(2) = \text{Cu}(2)]$. Two $\text{Cu}(3)$ octahedra share a common edge and alternate with a vacant octahedron along $[01\bar{1}]$ (Figs. 3a, b). The size of the vacant octahedron is smaller than that of the Cu octahedra as the former links to two V tetrahedra, above and below the sheet, which constrains the size of the vacant octahedron. The repeat distances of the two chains $[\text{Cu}(1) = \text{Cu}(2) = \text{Cu}(2)]$ and $[\text{Cu}(3) = \text{Cu}(3) = \square]$ (Fig. 3a) must be equal. As the vacant octahedron is smaller than the Cu octahedra, the $[\text{Cu}(3) = \text{Cu}(3) = \square]$ chain must increase its length relative to that of a chain of holosymmetric octahedra of similar size, whereas the $[\text{Cu}(1) = \text{Cu}(2) = \text{Cu}(2)]$ chain must decrease its length relative to that of a chain of holosymmetric octahedra of similar size. These changes occur *via* the orientation of the Jahn–Teller elongation of the occupied octahedra: $\text{Cu}(1)$ and $\text{Cu}(2)$ octahedra elongate orthogonal to $[01\bar{1}]$, thereby shortening the $[\text{Cu}(1) = \text{Cu}(2) = \text{Cu}(2)]$ chain in this direction, whereas the $\text{Cu}(3)$ octahedron elongates at an oblique angle to $[01\bar{1}]$, and hence the $[\text{Cu}(3) = \text{Cu}(3) = \square]$ chain is extended by the component of octahedron elongation parallel to $[01\bar{1}]$.

There is one unique V site tetrahedrally coordinated by O atoms, with a $\langle \text{V-O} \rangle$ distance of 1.725 Å. The V tetrahedron has one short bond $\text{V-O}(4) = 1.660$ Å. In order to satisfy its bond-valence requirements, the O(4) atom has two long bonds with $\text{Cu}(2)$ and $\text{Cu}(3)$.

Structure topology

The $\text{Cu}(1)$, $\text{Cu}(2)$ and $\text{Cu}(3)$ octahedra share six, three and five edges with adjacent octahedra to form an

TABLE 2. MISCELLANEOUS REFINEMENT DATA FOR TURANITE

| | |
|---|---|
| <i>a</i> (Å) | 5.3834(2) |
| <i>b</i> | 6.2736(3) |
| <i>c</i> | 6.8454(3) |
| α (°) | 86.169(1) |
| β | 91.681(1) |
| γ | 92.425(1) |
| <i>V</i> (Å ³) | 230.38(2) |
| Space group | $P\bar{1}$ |
| <i>Z</i> | 1 |
| Absorption coefficient (mm ⁻¹) | 13.38 |
| <i>F</i> (000) | 323.0 |
| <i>D</i> _{calc.} (g/cm ³) | 4.898 |
| Crystal size (mm) | 0.02 x 0.05 x 0.06 |
| Radiation/ filter | MoK α /graphite |
| 2 θ -range for data collection (°) | 59.93 |
| <i>R</i> (int) (%) | 0.8 |
| Reflections collected | 6381 |
| <i>F</i> _o > 4 σ <i>F</i> | 2686 |
| Independent reflections | 1346 |
| <i>F</i> _o > 4 σ <i>F</i> | 1332 |
| Refinement method | Full-matrix least-squares on <i>F</i> ² , fixed weights proportional to 1/ <i>σF</i> _o ² |
| Goodness of fit on <i>F</i> ² | 1.192 |
| Final <i>R</i> (obs) (%) [<i>F</i> _o > 4 σ <i>F</i>] | <i>R</i> ₁ = 2.2 |
| <i>R</i> indices (all data) (%) | <i>R</i> ₁ = 2.2 <i>WR</i> ₂ = 5.7 GoF = 1.192 |

TABLE 3. FINAL ATOM POSITIONS AND DISPLACEMENT PARAMETERS (Å²) FOR TURANITE

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> ₀₀ | <i>U</i> ₁₁ | <i>U</i> ₂₂ | <i>U</i> ₃₃ | <i>U</i> ₂₃ | <i>U</i> ₁₃ | <i>U</i> ₁₂ |
|----------------|-------------|------------|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| $\text{Cu}(1)$ | 0 | 1/2 | 0 | 0.00884(10) | 0.00821(18) | 0.00867(19) | 0.00937(19) | 0.00302(13) | 0.00157(13) | 0.00188(13) |
| $\text{Cu}(2)$ | -0.00879(5) | 0.15238(4) | 0.33553(4) | 0.00897(9) | 0.01027(15) | 0.00822(15) | 0.00849(15) | 0.00202(10) | 0.00262(10) | 0.00342(10) |
| $\text{Cu}(3)$ | -0.50426(5) | 0.32074(4) | 0.17404(4) | 0.00894(10) | 0.00786(15) | 0.00699(15) | 0.01183(16) | 0.00012(10) | -0.00061(10) | 0.00053(10) |
| <i>V</i> | -0.56313(7) | 0.80958(6) | 0.31396(5) | 0.00732(10) | 0.00783(17) | 0.00639(17) | 0.00786(17) | -0.00081(12) | 0.00104(12) | 0.00050(12) |
| O(1) | 0.1473(3) | -0.1188(3) | 0.4007(3) | 0.0104(3) | 0.0106(7) | 0.0099(7) | 0.0108(7) | 0.0014(6) | 0.0039(6) | 0.0030(6) |
| O(2) | -0.6197(3) | 0.6156(3) | 0.1464(3) | 0.0101(3) | 0.0115(7) | 0.0077(7) | 0.0114(7) | -0.0019(6) | -0.0002(6) | 0.0016(6) |
| O(3) | -0.6049(3) | -0.0228(3) | -0.2017(3) | 0.0106(3) | 0.0117(7) | 0.0081(7) | 0.0120(7) | 0.0002(6) | 0.0013(6) | 0.0007(6) |
| O(4) | -0.3827(3) | 0.7093(3) | 0.4952(3) | 0.0120(3) | 0.0148(8) | 0.0107(8) | 0.0102(7) | -0.0002(6) | -0.0009(6) | 0.0004(6) |
| O(5) | 0.1586(3) | 0.2236(3) | 0.0820(3) | 0.0100(3) | 0.0097(7) | 0.0108(8) | 0.0096(7) | -0.0000(6) | 0.0012(6) | 0.0016(6) |
| O(6) | -0.1633(3) | 0.4229(3) | 0.2514(2) | 0.0086(3) | 0.0088(7) | 0.0085(7) | 0.0087(7) | -0.0006(5) | 0.0006(5) | 0.0003(6) |
| H(1) | 0.193(8) | 0.119(5) | -0.012(5) | 0.043(12)* | | | | | | |
| H(2) | -0.185(6) | 0.529(4) | 0.346(4) | 0.01037(10)* | | | | | | |

* *U*_{iso}

interrupted sheet of octahedra (Fig. 3a). In this sheet, each vacant octahedron is surrounded by four *Cu*(2) octahedra and two *Cu*(3) octahedra, and is sandwiched between two *V* tetrahedra with their apices pointing away from the sheet (Fig. 4a). These sheets form a framework (Fig. 4b).

Hydrogen bonding

The bond-valence incident at the various anions from the *Cu* cations (Table 6) show O(5) and O(6) to be (OH)

TABLE 4. INTERATOMIc DISTANCES (Å) FOR TURANITE

| | | | | |
|---------------------|----|-----------------|---------------------|-----------------|
| <i>Cu</i> (1)–O(2) | x2 | 2.360(2) | <i>V</i> –O(1) | 1.770(2) |
| <i>Cu</i> (1)–O(5) | x2 | 2.004(2) | <i>V</i> –O(2) | 1.739(2) |
| <i>Cu</i> (1)–O(6) | x2 | <u>1.977(2)</u> | <i>V</i> –O(3) | 1.731(2) |
| < <i>Cu</i> (1)–O> | | 2.114 | <i>V</i> –O(4) | <u>1.660(2)</u> |
| | | | < <i>V</i> –O> | 1.725 |
| <i>Cu</i> (2)–O(1) | | 1.948(2) | <i>Cu</i> (3)–O(2) | 1.971(2) |
| <i>Cu</i> (2)–O(1)a | | 1.969(2) | <i>Cu</i> (3)–O(2)b | 2.316(2) |
| <i>Cu</i> (2)–O(3) | | 2.381(2) | <i>Cu</i> (3)–O(3) | 1.979(2) |
| <i>Cu</i> (2)–O(4) | | 2.525(2) | <i>Cu</i> (3)–O(4) | 2.355(2) |
| <i>Cu</i> (2)–O(5) | | 1.994(2) | <i>Cu</i> (3)–O(5) | 1.989(2) |
| <i>Cu</i> (2)–O(6) | | <u>1.966(2)</u> | <i>Cu</i> (3)–O(6) | <u>1.987(2)</u> |
| < <i>Cu</i> (2)–O> | | 2.131 | < <i>Cu</i> (3)–O> | 2.100 |

a: $-x, -y, -z + 1$; b: $-x-1, -y+1, -z$

TABLE 5. HYDROGEN BONDING IN TURANITE

| D–H...A | D–H (Å) | H...A (Å) | D...A (Å) | ∠ (DHA) (°) | D–A (Å) |
|------------------|----------|-----------|-----------|-------------|----------|
| O(5)–H(1)...O(3) | 0.98(10) | 1.99(2) | 2.915(3) | 156(4) | 2.915(3) |
| O(6)–H(2)...O(4) | 0.97(10) | 1.94(2) | 2.847(2) | 153(3) | 2.847(2) |

groups. The H atoms associated with the (OH) groups were located in the refinement (Table 3), and Table 5 show the hydrogen-bond arrangements. The H(1) and H(2) atoms are hydrogen-bonded to the O(3) and O(4) atoms of the adjacent layer (Fig. 5), with an H...O distance of 1.99 and 1.94 Å, respectively.

RELATED STRUCTURES

Hawthorne & Schindler (2000) examined the principles involved in the structures of hydroxy-hydrated copper (and zinc) minerals based on decorated $[Cu^{2+}\phi_2]_N$ sheets (ϕ : any anion of the sheet). Hawthorne & Sokolova (2002) refined the crystal structure of simonkolleite, $Zn_5(OH)_8Cl_2(H_2O)$, and considered its structure and some other structures in which there are vacancies at some of the octahedrally coordinated sites

TABLE 6. BOND-VALENCE* (*vu*) TABLE FOR TURANITE

| | <i>Cu</i> (1) | <i>Cu</i> (2) | <i>Cu</i> (3) | <i>V</i> | H(1) | H(2) | Σ |
|-------|----------------------|----------------|----------------|----------|------|------|-------|
| O(1) | | 0.471 0.441 | | 1.062 | | | 1.974 |
| O(2) | 0.149 ² ! | | 0.439 0.167 | 1.162 | | | 1.917 |
| O(3) | | 0.141 | 0.428 | 1.190 | 0.13 | | 1.889 |
| O(4) | | 0.099 | 0.151 | 1.473 | | 0.14 | 1.863 |
| O(5) | 0.397 ² ! | 0.409 | 0.415 | | 0.87 | | 2.091 |
| O(6) | 0.431 ² ! | 0.445 | 0.418 | | | 0.86 | 2.154 |
| Total | 1.954 | 2.006 | 2.018 | 4.887 | 1.00 | 1.00 | |

* bond-valence parameters from Brown (1981)

TABLE 7. MINERALS BASED ON CLOSE-PACKED DECORATED $[M^{2+}\phi_2]_N$ SHEETS, ($M = Cu^{2+}, Zn$)

| Mineral | Formula | <i>a</i> (Å) α (°) | <i>b</i> (Å) β (°) | <i>c</i> (Å) γ (°) | Space group | Structure | Ref. |
|---------------|--|------------------------|------------------------|------------------------|-------------|-----------|------|
| Turanite | $[Cu_5(VO_4)_2(OH)_4]$ | 5.3834(2) 86.169(1) | 6.2736(3) 91.681(1) | 6.8454(3) 92.425(1) | $P\bar{1}$ | Framework | (1) |
| Cornubite | $[Cu_5(AsO_4)_2(OH)_4]$ | 6.121(1) 92.93(1) | 6.251(1) 111.30(1) | 6.790(1) 107.47(1) | $P\bar{1}$ | Framework | (2) |
| Simonkolleite | $[Zn_5(OH)_8Cl_2(H_2O)]$ | 6.3412(3) – | <i>a</i> – | 23.646(1) – | $R\bar{3}m$ | Sheet | (3) |
| Cianciullite | $Mn(Mg,Mn)_2Zn_2(OH)_{12}(H_2O)_{2-4}$ | 15.405(3) – | 6.344(1) 101.23(2) | 5.562(2) – | $C2/m$ | Sheet | (4) |
| Gordaite | $Na[Zn_4(SO_4)(OH)_6Cl](H_2O)_6$ | 8.3556(3) – | <i>a</i> – | 13.025(1) – | $P3$ | Sheet | (5) |
| Bechererite | $[Zn_7Cu^{2+}SiO(OH)_3(SO_4)(OH)_{13}]$ | 8.319(2) – | <i>a</i> – | 7.377(1) – | $P\bar{3}$ | Framework | (6) |
| Ramsbeckite | $(Cu^{2+},Zn)_{15}(OH)_{22}(SO_4)_4(H_2O)_6$ | 16.088(4) – | 15.576(4) 90.22(2) | 7.102(2) – | $P2_1/a$ | Framework | (7) |

References: (1) This work; (2) Sieber *et al.* (1984); (3) Hawthorne & Sokolova (2002); (4) Grice & Dunn (1991); (5) Adiwidjaja *et al.* (1997); (6) Hoffmann *et al.* (1997); (7) Effenberger (1988)

in the sheet, the “interrupted” sheets. For simonkolleite, ciangiullite, $Mn(Mg,Mn)_2Zn_2(OH)_{10}(H_2O)_{2-4}$, gordaite, $Na[Zn_4(SO_4)(OH)_6Cl](H_2O)_6$, namuwite, $(Zn,Cu^{2+})_4(SO_4)(OH)_6(H_2O)_4$, bechererite, $Zn_7Cu^{2+}SiO(OH)_3(SO_4)(OH)_{13}$, chalcophyllite, $[Cu^{2+}_9Al(AsO_4)_2(OH)_{12}(H_2O)_6](SO_4)_{1.5}(H_2O)_{12}$, ramsbeckite, $(Cu^{2+}_{13},Zn_2)(OH)_{22}(SO_4)_4(H_2O)_6$, chalcophanite, $ZnMn_3O_7(H_2O)_3$, and claringbullite, $Cu^{2+}_4Cl(OH)_6(Cl_{0.29}(OH)_{0.71})$, they rewrote the formulae by incorporating octahedrally coordinated vacancies and by identifying the decorating oxyanions and their mode of attachment to the sheet, and showed that all these structures have a decorated $(^{6l}M\phi_2)_N$ sheet as the structural unit.

The structure of turanite fits into this scheme if we write the formula in the following way: $[^{6l}(Cu^{2+}_3\Box)]^{4l}[V^{5+}O_4]_2(OH)_4$. Each tetrahedron links to three anions of one sheet (Fig. 4a), and hence we can write the (VO_4) tetrahedra as ϕ_3 (ϕ = any anion of the sheet). Hence the above formula reduces to $[(Cu_3\Box)\phi_{6+2}] =$

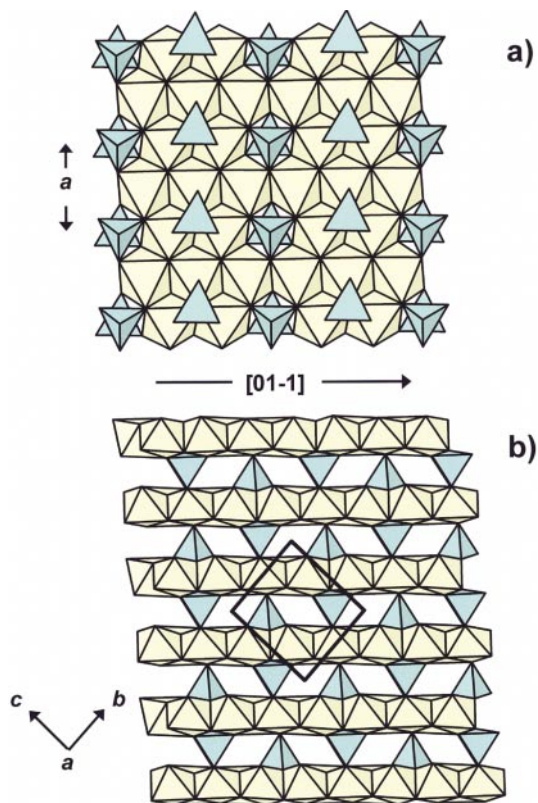


FIG. 4. The crystal structure of turanite: (a) the sheet of Cu octahedra and V tetrahedra viewed down [011]; (b) the mixed octahedron-tetrahedron framework viewed down [100]; Cu octahedra are yellow, V tetrahedra are green.

$[M_4\phi_8] = [M\phi_2]_4$, where $M = ^{6l}(Cu, \Box)$ and ϕ represents octahedron ligands. Thus turanite has a structure based on a decorated $(^{6l}M\phi_2)_N$ sheet.

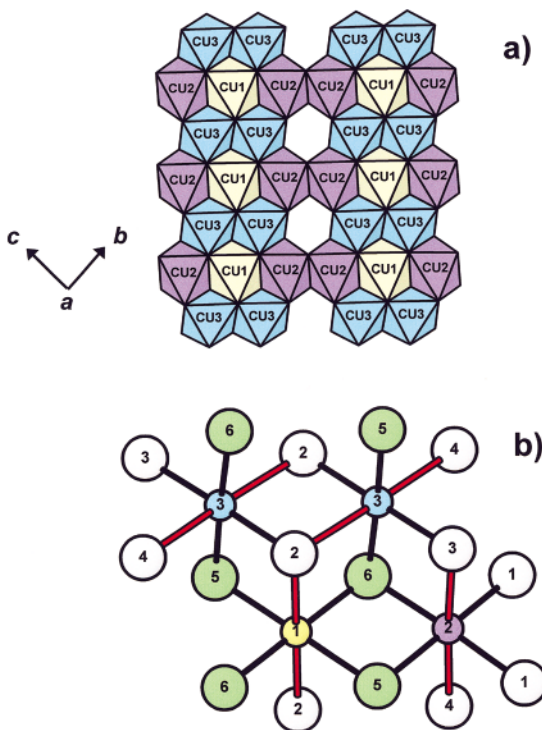


FIG. 3. The crystal structure of turanite: (a) the sheet of Cu octahedra viewed down [100]; (b) coordination of Cu sites viewed down [100]; Cu(1), Cu(2) and Cu(3) atoms and octahedra are yellow, mauve and blue; O atoms are white, O atoms of (OH) groups are green, Cu-φ short and long bonds are black and red, respectively.

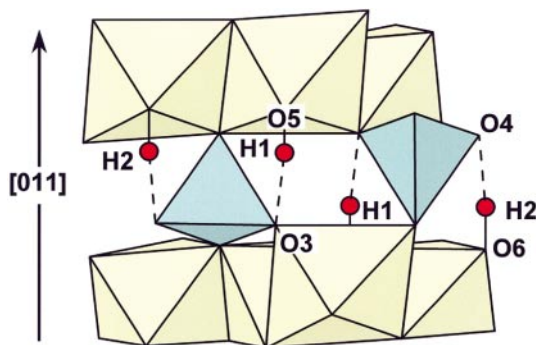


FIG. 5. The hydrogen-bond arrangement in turanite. Legend as in Figure 4; H atoms are red circles, hydrogen bonds are dashed lines.

We will consider crystal structures of simonkollite, cianciulliite and gordaitite (Table 7), with the same type of close-packed decorated $(^{[6]}M\phi_2)_N$ sheets, and cornubite, bechererite and ramsbeckite, in which the particular sheets are part of a framework.

Simonkollite

The $(Zn\phi_6)$ octahedra (ϕ : O, OH, Cl) form a dioctahedral sheet of edge-sharing octahedra similar to that observed in dioctahedral micas. On each side of the vacant octahedron, a $(Zn\phi_4)$ tetrahedron is attached to

three anions of the sheet and points away from the sheet (Fig. 6a). The decorated sheet can be written as $[M_3 \square (T\phi_4)_2 \phi_2]$ where $M = ^{[6]}Zn$, $T = ^{[4]}Zn$ and $\phi = OH, Cl$. The sheets are held together by hydrogen bonding from (OH) groups of one sheet to Cl anions of adjacent sheets, and to interstitial (H_2O) groups.

Cianciulliite

Cianciulliite has an interrupted sheet of the form $[M\phi_2]_4$, where $M = Mn^{2+}$, and $(Mg_{0.5}Mn^{2+}_{0.5})$ and \square (Hawthorne & Sokolova 2002). Each vacancy in the

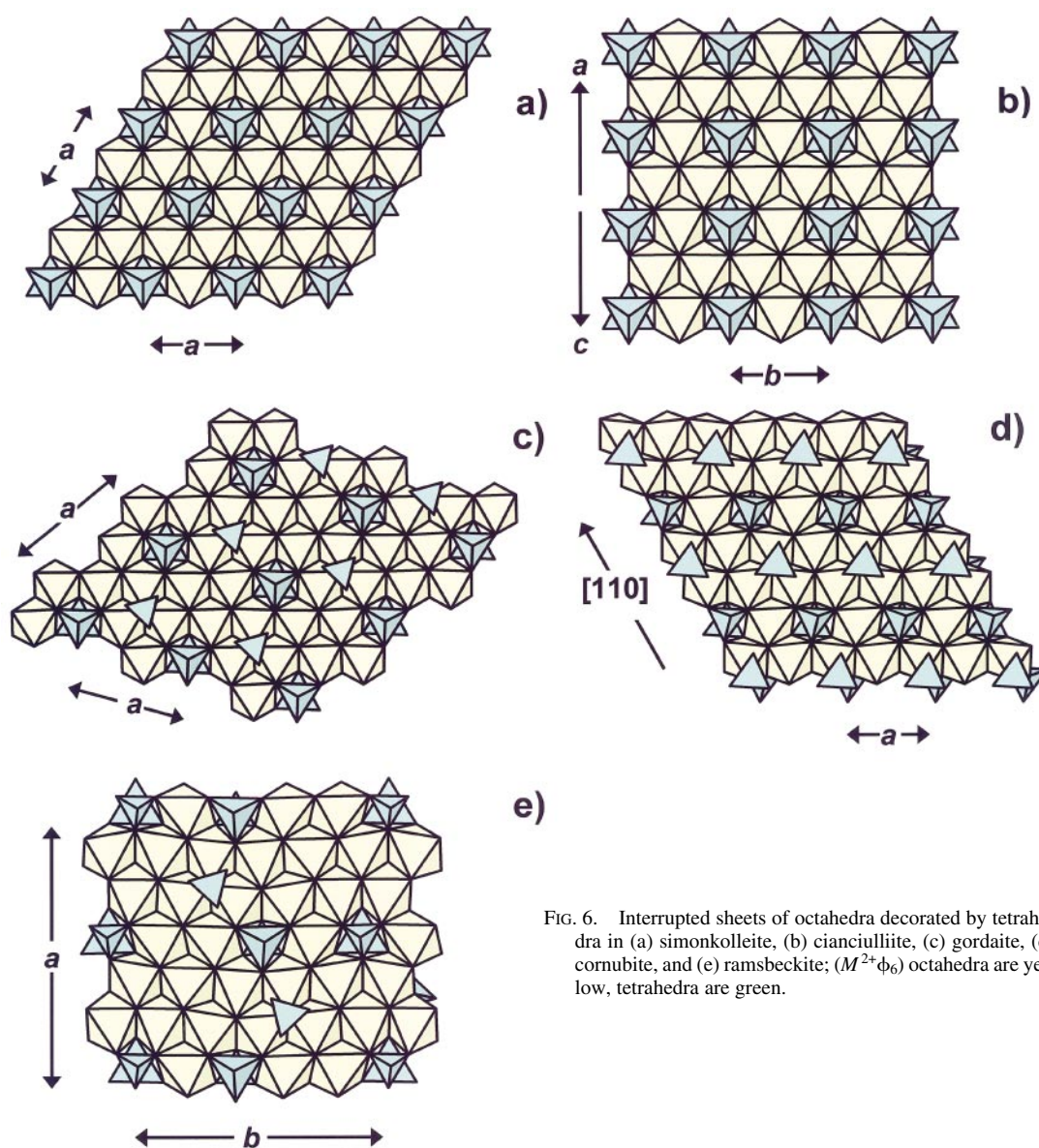


FIG. 6. Interrupted sheets of octahedra decorated by tetrahedra in (a) simonkollite, (b) cianciulliite, (c) gordaitite, (d) cornubite, and (e) ramsbeckite; $(M^{2+}\phi_6)$ octahedra are yellow, tetrahedra are green.

sheet is occluded by two $Zn(OH)_4$ tetrahedra, each of which are attached to the sheet by three ligands (Fig. 6b), in the same fashion as in simonkolleite. The sheets are held together by hydrogen bonding from (OH) groups of one sheet to O atoms of adjacent sheets, and to interstitial (H_2O) groups.

Gordaite

Gordaite has vacancies in the sheet of octahedra, and one quarter of the Zn is tetrahedrally coordinated. In the crystal structure of gordaite, six Zn cations are octahedrally coordinated, and two Zn cations are tetrahedrally coordinated. Each $\{Zn(OH)_4\}$ group links to three sheet anions, and each (SO_4) tetrahedron links to one sheet anion (Fig. 6c). The sheets are held together by hydrogen bonding from (OH) groups of one sheet to O atoms of the interstitial [6]-coordinated interstitial Na atoms.

Bechererite

In bechererite, there are six octahedrally coordinated (Zn, Cu^{2+}) cations, every seventh octahedron is vacant, and there are two tetrahedrally coordinated Zn cations. The topology of the $(^{6l}M\phi_2)_N$ sheet in bechererite is the same as in gordaite (Fig. 6c), but chemically they are different. In bechererite, there are (SO_4) tetrahedra on one side and (SiO_4) tetrahedra on the other side of the sheet. The tetrahedrally coordinated Zn forms a $[T_2O_7]$ pyro-group in which all non-bridging bonds involve anions of the sheet (*i.e.*, the pyro-group links adjacent sheets into a framework).

Cornubite

In spite of their identical stoichiometry (Table 7), turanite and cornubite have $(^{6l}M\phi_2)_N$ sheets of different topology resulting from different patterns of vacancies within the $[Cu\phi_2]$ sheet ($\phi = O, OH$) (Figs. 4a, 6d). On each side of the vacant octahedron, an ($As\phi_4$) tetrahedron is attached to three anions of the sheet and points away from the sheet. The sheets are held together by hydrogen bonding from (OH) groups of one sheet to O anions of adjacent sheets. The $[Cu\phi_2]$ sheets and ($As\phi_4$) tetrahedra link together to form a framework similar to that of turanite.

Ramsbeckite

There is a $[Cu\phi_2]$ sheet in the crystal structure of ramsbeckite (Fig. 6e), together with two Zn cations per formula unit in tetrahedral coordination. The ($Zn\phi_4$) tetrahedron shares three anions with the sheet and the fourth anion with an (SO_4) group of an adjacent sheet, forming a framework. There are two types of (SO_4) groups, and half of them share an O atom with ($Zn\phi_4$) tetrahedra. There is extensive hydrogen bonding between $[Cu\phi_2]$ sheets involving interstitial (H_2O) groups.

SUMMARY

Turanite, $Cu^{2+}_5(V^{5+}O_4)_2(OH)_4$, is a framework structure with an interrupted sheet of Cu octahedra as the structural unit. The crystal structure of turanite is related to the framework structures of cornubite, bechererite and ramsbeckite and the sheet structures of simonkolleite, gordaite and ciangiullite. Its composition is in accordance with the structural refinement, and this work has confirmed the status of turanite as a valid mineral species.

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