

Tangdanite, a new mineral species from the Yunnan Province, China and the discreditation of ‘clinotyrolite’

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ABSTRACT

Tangdanite, ideally $\text{Ca}_2\text{Cu}_9(\text{AsO}_4)_4(\text{SO}_4)_{0.5}(\text{OH})_9 \cdot 9\text{H}_2\text{O}$ and monoclinic, is a new mineral species (IMA No. 2011-096) occurring in the Tangdan and Nanniping mines, southeast Dongchuan copper mining district, Dongchuan County, Kunming City Prefecture, Yunnan Province, P. R. China (26°11'N 103°51'E). The mineral is found in the oxidized zone (gossan) of an As-bearing Cu sulfide deposit and is clearly of supergene origin. Associated minerals are chalcopyrite, bornite, chalcocite, covellite, tennantite, enargite, cuprite, malachite, azurite, copper and brochantite. Crystals form radiating or foliated aggregates of flaky crystals up to 3 mm, flattened parallel to (100) and elongated along [001]. It is emerald green with a light green streak, translucent and has a pearly to silky lustre. It is sectile having perfect cleavage on {100} although neither parting nor fracture was observed. No fluorescence in long- or short-wave ultraviolet radiation was observed. The hardness is VHN_{50} 42.0–43.6, mean 42.8 kg mm^{-2} ($2\text{--}2\frac{1}{2}$ on the Mohs scale). The density measured by pycnometry is 3.22 g cm^{-3} (Ma *et al.*, 1980). The calculated density from the empirical chemical formula is 3.32 g cm^{-3} . The compatability index gives $1 - (\text{K}_p/\text{K}_c) = -0.041$ (good). The empirical formula (based on 36 O a.p.f.u) of tangdanite is $\text{Ca}_{2.05}\text{Cu}_{9.08}(\text{As}_{1.03}\text{O}_4)_4(\text{S}_{0.63}\text{O}_4)_{0.5}(\text{OH})_9 \cdot 9\text{H}_{2.04}\text{O}$. The simplified formula is $\text{Ca}_2\text{Cu}_9(\text{AsO}_4)_4(\text{SO}_4)_{0.5}(\text{OH})_9 \cdot 9\text{H}_2\text{O}$. The strongest five reflections in the X-ray powder-diffraction pattern [d in Å (hkl)] are: 4.782(100) ($\bar{3}$ 1 1), 4.333(71) (6 0 2), 5.263(54) ($\bar{2}$ 0 2), 3.949(47) (8 0 2) and 2.976(46) ($\bar{1}$ 5 1). The unit-cell parameters are $a = 54.490(9)$, $b = 5.5685(9)$, $c = 10.4690(17)$ Å, $\beta = 96.294(3)^\circ$, $V = 3157.4(9) \text{ Å}^3$, $Z = 4$. Its structure was solved and refined in space group $C2/c$, with $R = 0.110$.

KEYWORDS: tangdanite, new mineral species, ‘clinotyrolite’, Dongchuan copper mining district, Yunnan, China.

Introduction

TANGDANITE as a mineral has not hitherto been submitted to or approved by the International Mineralogical Association (IMA). The *Mineralogical Magazine*’s 31st New Mineral List indicated ‘clinotyrolite’ to be an IMA-approved mineral. However, in the IMA list of minerals, ‘clinotyrolite’ is marked as a mineral

without approval by the Commission on New Minerals, Nomenclature and Classification (CNMNC). Ma *et al.* (1980) described ‘clinotyrolite’ as a new species but, as this was prior to China joining the IMA, the mineral was not submitted to nor recognized by the IMA. Ma, together with other colleagues (Liao *et al.*, 1996) did further work on this mineral but again did not submit it for approval. The reason given by Ma *et al.* (1980) for the name was that the authors believed it to be similar to tyrolite (then thought to be orthorhombic) while this mineral is

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monoclinic. The name they gave implies that it is a monoclinic polymorph of tyrolite. Li *et al.* (2004) also reference this mineral as being a monoclinic variety of tyrolite. Subsequently, Krivovichev *et al.* (2006) established that tyrolite was in fact monoclinic but they did not examine 'clinotyrolite' as no type material was available at the time. Nevertheless, this meant that the name 'clinotyrolite' seemed superfluous unless it was shown to be distinct from tyrolite. Furthermore, the Past Chair of the CNMNC, Ernst Burke, stated (pers. comm. on Mindat.org on 21 June 2004), "Clinotyrolite has been published without CNMNC approval. It might well be a separate phase."

The crystal structure of tangdanite was first described by Ma *et al.* (1980) using a sample from Dongchuan, China, assuming the formula $\text{Ca}_2\text{Cu}_9(\text{AsO}_4, \text{SO}_4)_4(\text{OH}, \text{O})_{10} \cdot 10\text{H}_2\text{O}$ and $Z = 2$. They determined the space group to be *Pa* or *P2/a*. While their chemical analysis is similar to that in older references to tyrolite, it needs to be noted that the mineral and tyrolite were not analysed for the presence of CO_2 . Subsequently, it has been shown by Krivovichev *et al.* (2006) that CO_2 is a determinative chemical characteristic of tyrolite while SO_4 is not considered important in the structure. Advances in technology now permit a more detailed determination of these matters.

Despite these advances, a fundamental problem remained in that type material of 'clinotyrolite' was not available to the scientific community. While its exact location was known to Ma, it was not deemed significant to describe it further as it was generally believed to be tyrolite once it was determined that all tyrolite is monoclinic (Krivovichev *et al.*, 2006). It was only after Fu Xiaotu pursued the matter with Li Guowu and Shi Nicheng that the potential significance of the type material came to the attention of Ma. The type material was located and made available for re-examination. The name given here is for the type locality.

Tangdanite was found to be devoid of CO_2 and it was discovered that SO_4 is important to its structure. Furthermore, tangdanite has a different $\text{Ca}:\text{Cu}:\text{OH}:\text{H}_2\text{O}$ ratio from that of tyrolite.

This paper establishes that 'clinotyrolite' constitutes a distinct species. The name 'clinotyrolite' is discredited and the new mineral tangdanite and its name have been approved by the CNMNC of the IMA (IMA 2011-96). Holotype specimens of tangdanite are deposited in the collections of the Geological Museum of China, Beijing, P. R.

China, catalogue number M11802 and in the Canadian Museum of Nature, Gatineau, Quebec, Canada, catalogue number CMNMC 86550.

Occurrence

Tangdanite occurs in the Tangdan and Nanniping mines, southeast Dongchuan copper mining district, Dongchuan County, Kunming City Prefecture, Yunnan Province, P. R. China ($26^\circ 11' \text{N}$ $103^\circ 51' \text{E}$). It is found in the oxidized zone (gossan) of an As-bearing Cu sulfide deposit and is clearly of supergene origin. Minerals associated with tangdanite are chalcopyrite, bornite, chalcocite, covellite, tennantite, enargite, cuprite and secondary mineral associates are malachite, azurite, copper and brochantite.

The Nanniping copper mine is located on the southern limb of the Huangcaoling syncline. The ore-bearing layer is in the Luoxue dolomite of the Kunyang Group. Copper mining is from veins and is disseminated in lenticular deposits. Tangdanite is found in the lenticular deposits, distributed within the ore veins (Ma *et al.*, 1980).

Physical and optical properties

Crystals form radiating or foliated aggregates of flaky crystals up to 3 mm in size (Fig. 1). According to Fig. 2, crystals are flattened parallel to (100) and elongated along [001]. Tangdanite has a tabular habit with forms {100}, {010}, {001} and {013}. No twinning was observed. Individual grains of tangdanite attain sizes of about 0.5 mm. Tangdanite is emerald green to dark grey with a light-green streak, translucent



FIG. 1. Tangdanite crystals from Dongchuan. Field of view is 6 mm.

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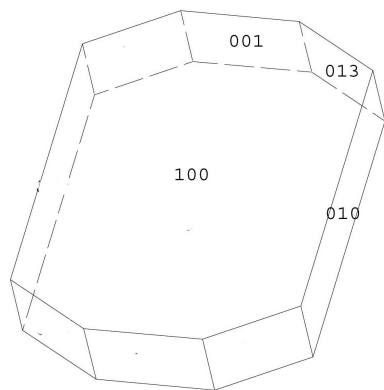


FIG. 2. Tangdanite crystal drawn using the *SHAPE* program.

and has a pearly to silky lustre. Cleavage is perfect on {100}. It is sectile and is without an observed parting or fracture. The Vickers microhardness is 42.8 kg mm⁻², ranging from 42.0–43.6 kg mm⁻² (load 50 g), corresponding to 2–2½ on the Mohs scale. No fluorescence in long- or short-wave ultraviolet light was observed. The density, calculated from the empirical chemical formula, is 3.32 g cm⁻³ and 3.22 g cm⁻³ measured by pycnometry (Ma *et al.*, 1980). No error was reported but there is insufficient type material remaining to repeat the measurement by pycnometry. The Gladstone-Dale relationship (Mandarino, 2007) gives 1 – (K_p/K_c) = –0.041 (good).

Tangdanite is biaxial(–), $\alpha = 1.666$, $\beta = 1.686$, $\gamma = 1.694$ in white light. 2V(meas.) = 65–66°, 2V(calc.) = 64°. The dispersion is both $r > v$ and $r < v$, but weak. The orientation is $Y = b$; $Z \wedge a =$

3°–4°; $X \wedge c = 7^\circ$ –8°. It is also weakly pleochroic, $Z =$ medium green and $Y =$ yellow green.

Chemical composition

Chemical analyses were performed with a JEOL-733 electron microprobe (WDS mode). Accelerating voltage and specimen current were kept at 20 kV and 10 nA. The beam diameter was 10 µm. The following minerals and synthetic materials were used as standards: diopside for Ca, cuprite for Cu, GaAs for As and pentlandite for S. An infrared (IR) spectrum analysis for CO₂ was obtained, which determined that bands for CO₃^{2–} are completely absent in tangdanite. Water was not determined directly because of the paucity of available material and the content was calculated by difference. Analytical data are given in Table 1.

An average of ten measurements of the composition of tangdanite gave the empirical formula Ca_{2.05}Cu_{9.08}(As_{1.03}O₄)₄(S_{0.63}O₄)_{0.5}(OH)₉·9H_{2.04}O, on the basis of 36 oxygen a.p.f.u. (atoms per formula unit). The simplified formula is Ca₂Cu₉²⁺(AsO₄)₄(SO₄)_{0.5}(OH)₉·9H₂O, which requires CaO 7.14, CuO 45.57, As₂O₅ 29.26, SO₃ 2.55, H₂O 15.48, total 100.00 wt.%.

Crystallography and X-ray powder diffraction data

The X-ray powder diffraction (XRPD) data collection was performed on a SMART APEX-CCD area detector diffractometer using MoK α radiation, 45 kV, 35 mA. A new method was used by taking powder diffraction Debye images with a 0.2 mm × 0.1 mm × 0.06 mm crystal grain and repeated rotation with $\Delta\omega = 10^\circ$. The exposure

TABLE 1. Chemical composition of tangdanite (10 analyses).

Constituent	Tangdanite			Comparison with previous analyses	
	(wt.%)	Range	Stand. dev.	(wt.%) (Li <i>et al.</i> , 2004)	(wt.%) (Ma <i>et al.</i> , 1980)
CaO	7.29	7.13–7.46	0.05	7.13	7.24
CuO	45.71	45.06–47.53	0.3	44.58	46.04
As ₂ O ₅	29.82	29.03–30.88	0.35	30.91	28.09
SO ₃	1.60	1.17–1.86	0.2	0.75	1.28
H ₂ O	15.58*			16.63	17.63
Total	100.00			100.00	100.28

* By difference.

TABLE 2. X-ray powder diffraction data for tangdanite (Å). The most intense diffraction lines are shown in bold.

I_{rel}	$d_{\text{meas.}}$	$d_{\text{calc.}}$	$h\ k\ l$	I_{rel}	$d_{\text{meas.}}$	$d_{\text{calc.}}$	$h\ k\ l$
54	5.263	5.219	$\bar{2}\ 0\ 2$	7	2.277	2.277	$\bar{14}\ 0\ 4$
100	4.782	4.805	$\bar{3}\ 1\ 1$	3	2.173	2.173	0 2 3
71	4.333	4.311	6 0 2	10	2.084	2.083	$\bar{18}\ 0\ 4$
47	3.949	3.925	8 0 2	8	1.883	1.882	20 2 1
5	3.707	3.713	9 1 1	7	1.818	1.821	25 1 2
15	3.530	3.527	$\bar{7}\ 1\ 2$	24	1.744	1.746	$\bar{4}\ 0\ 6$
20	3.350	3.338	$\bar{9}\ 1\ 2$	9	1.692	1.692	$\bar{19}\ 1\ 5$
12	3.129	3.133	$\bar{11}\ 1\ 2$	20	1.644	1.644	$\bar{15}\ 3\ 1$
46	2.976	2.982	$\bar{15}\ 1\ 1$	3	1.546	1.546	26 0 4
13	2.843	2.842	$\bar{7}\ 1\ 3$	5	1.502	1.502	$\bar{19}\ 1\ 6$
41	2.631	2.627	4 2 1	7	1.476	1.475	$\bar{27}\ 1\ 5$
11	2.527	2.526	$\bar{8}\ 2\ 1$	10	1.436	1.437	18 0 6
9	2.449	2.452	$\bar{10}\ 0\ 4$	6	1.383	1.383	37 1 1
29	2.368	2.369	$\bar{12}\ 0\ 4$	2	1.320	1.320	35 1 3

time was 60 s and very clear Debye ring images were obtained using the method of Li *et al.* (2005). The powder diffraction pattern and diffraction data were obtained using *GADDS* software (for WNT 4·1·14, Bruker) and data are reported in Table 2.

The strongest five reflections in the XRPD pattern [d in Å(hkl)] are: 4.782(100) ($\bar{3}\ 1\ 1$), 4.333(71) (6 0 2), 5.263(54) ($\bar{2}\ 0\ 2$), 3.949(47) (8 0 2) and 2.976(46) ($\bar{15}\ 1\ 1$). The XRPD refined unit-cell parameters are $a = 54.4426(78)$, $b = 5.5750(10)$, $c = 10.4754(15)$ Å, $\beta = 96.240(10)^\circ$ and $V = 3160.6(49)$ Å³. The $a:b:c$ ratio is 9.765:1:1.879.

Refinement of crystal structure

Single-crystal experiments were carried out using a Bruker Smart CCD diffractometer with a 0.2 mm × 0.1 mm × 0.06 mm grain and a 2.4 kW

sealed-tube X-ray source (MoK α X-radiation, $\lambda = 0.71073$ Å) operating at 45 kV and 35 mA. A hemisphere of intensity data was collected at room temperature in 1265 frames with ω scans (frame width 0.30° and exposure time 10 s per frame). The range of reciprocal space was $-56 \leq h \leq 68$, $-6 \leq k \leq 6$, $-13 \leq l \leq 13$. A total of 7275 diffraction measurements was collected. Intensity was obtained from images and corrected for LP using *SAINT* (Bruker) and absorption using the Bruker program *SADABS*. Only diffraction data with $F_o > 3\sigma(F_o)$ were considered as observed and after merging, a total of 3172 independent reflections [$R(\text{int}) = 0.061$] was used for structure determination and refinement (Table 3). Tangdanite cell parameters are $a = 54.490(9)$, $b = 5.5685(9)$, $c = 10.4690(17)$ Å, $\beta = 96.294(3)^\circ$ and $V = 3157.4(9)$ Å³, $Z = 4$.

The space group of tangdanite is proposed by the *XPREP* software package (in *SHELXTL* 5.1

TABLE 3. Crystallographic data and refinement parameters for tangdanite.

Space group	$C2/c$	Wavelength	0.71073 Å
a (Å)	54.490(9)	Absorption coefficient	10.690 mm ⁻¹
b (Å)	5.5685(9)	Crystal size	0.06 × 0.1 × 0.2 mm
c (Å)	10.4690(17)	Theta range for data collection	2.26 to 26.37°
β (°)	96.294(3)	Reflections collected	7275
V (Å ³)	3157.4(9)	Independent reflections	3172 [$R(\text{int}) = 0.0614$]
Z	4	R indices [$I > 2\sigma(I)$]	$R1 = 0.1143$, $wR2 = 0.2806$
D_{calc}	3.416 g cm ⁻³	Goodness-of-fit on F^2	1.207

TABLE 4. Atom coordinates and anisotropic displacement parameters ($\text{\AA}^2$) for tangdanite.

Atom	Occupancy	x/a	y/b	z/c	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1		0.17592(9)	0.2514(9)	0.1765(4)	0.034(3)	0.022(2)	0.021(2)	0.0000(19)	0.0037(18)	0.0014(18)
Cu1		0	1.00000	0	0.042(2)	0.0170(19)	0.0132(17)	0.0072(16)	0.0058(15)	-0.0002(14)
Cu2		0.02611(5)	0.5359(5)	-0.0468(2)	0.0337(16)	0.0144(13)	0.0107(11)	0.0031(10)	0.0058(10)	0.0009(9)
Cu3		0.07192(5)	0.1816(5)	0.1177(2)	0.0282(15)	0.0195(14)	0.0141(12)	0.0014(10)	0.0041(10)	0.0055(10)
Cu4		0.11869(5)	0.4684(5)	0.2545(3)	0.0247(14)	0.0169(14)	0.0217(13)	0.0017(10)	0.0012(10)	-0.0026(10)
Cu5		0.11907(5)	0.1666(5)	-0.0039(2)	0.0273(15)	0.0194(14)	0.0140(12)	0.0009(10)	0.003(1)	-0.0007(10)
As1		0.06795(4)	-0.2816(4)	0.30673(19)	0.0256(12)	0.0150(11)	0.0120(9)	0.0000(8)	0.0025(8)	-0.0001(8)
As2		0.15464(4)	0.6985(4)	0.0031(2)	0.0289(12)	0.0167(11)	0.0155(10)	-0.0014(9)	0.0032(8)	0.0010(8)
Si	0.26	0.2333(8)	0.151(5)	0.040(3)	0.10(4)	0.028(17)	0.04(2)	0.022(17)	0.012(18)	0.022(14)
O1(H)		0.0150(3)	0.846(3)	-0.1492(13)	0.035(9)	0.022(8)	0.008(6)	0.002(7)	0.002(6)	-0.005(6)
O2(H)		0.0094(3)	0.702(3)	0.0802(13)	0.031(9)	0.022(8)	0.008(6)	0.003(6)	0.006(6)	-0.002(6)
O3(H)		0.0379(3)	0.271(3)	0.0695(13)	0.019(8)	0.034(9)	0.009(6)	0.001(6)	0.006(5)	0.004(6)
O4		0.0628(3)	0.010(3)	0.2705(15)	0.035(9)	0.016(8)	0.024(8)	-0.001(6)	0.009(6)	0.007(6)
O5		0.0403(3)	-0.419(3)	0.3054(13)	0.034(9)	0.035(9)	0.007(6)	-0.001(7)	0.003(6)	0.004(6)
O6		0.0840(3)	-0.291(3)	0.4561(14)	0.030(9)	0.020(8)	0.019(7)	0.004(6)	0.009(6)	0.002(6)
O7		0.0843(3)	-0.428(3)	0.2029(16)	0.021(8)	0.020(8)	0.035(9)	-0.005(6)	0.010(6)	-0.009(7)
O8(W)	0.57	0.0658(8)	-0.206(7)	0.008(5)	0.08(3)	0.04(2)	0.09(4)	0.01(2)	0.02(3)	0.03(2)
O9		0.1076(3)	0.155(3)	0.1669(12)	0.026(8)	0.022(8)	0.007(6)	0.000(6)	0.006(5)	-0.005(6)
O10(W)	0.67	0.0977(7)	-0.214(7)	-0.048(4)	0.07(3)	0.05(2)	0.06(3)	-0.008(17)	-0.014(18)	0.008(18)
O11(H)		0.1264(3)	0.213(3)	-0.1781(13)	0.039(9)	0.016(8)	0.009(6)	0.001(6)	0.012(6)	0.001(5)
O12		0.1372(3)	0.502(3)	0.0744(17)	0.055(12)	0.018(9)	0.032(9)	-0.015(8)	0.021(8)	-0.009(7)
O13		0.1506(3)	0.984(3)	0.0468(15)	0.015(7)	0.029(9)	0.026(8)	-0.003(6)	-0.001(6)	-0.003(7)
O14		0.1497(3)	0.679(3)	-0.1636(13)	0.026(8)	0.043(10)	0.008(6)	-0.002(7)	-0.001(6)	0.002(6)
O15		0.1840(3)	0.619(3)	0.0561(15)	0.039(10)	0.035(10)	0.022(8)	0.003(8)	0.004(7)	-0.014(7)
O16(W)		0.2064(4)	0.403(4)	0.3388(17)	0.047(12)	0.057(14)	0.026(9)	-0.012(10)	0.001(8)	-0.003(9)
O17(W)		0.1832(4)	-0.112(4)	0.301(2)	0.055(13)	0.039(12)	0.049(12)	0.011(10)	0.006(10)	0.007(10)
O18(W)		0.2095(5)	0.118(6)	0.060(3)	0.061(19)	0.10(3)	0.11(2)	0.017(15)	0.021(15)	-0.03(2)
O19	0.49	0.2468(16)	-0.05(2)	0.138(7)	0.14(7)	0.47(15)	0.05(4)	0.03(7)	-0.02(4)	-0.15(6)
O20	0.86	0.2502(12)	0.111(19)	-0.091(10)	0.11(6)	0.31(10)	0.57(13)	-0.02(5)	-0.09(6)	-0.04(9)

for NT, Bruker) on the basis of extinction conditions. Mean $|E^2 - 1| = 0.966$, implies that the structure is centrosymmetric. The crystal structure was solved by direct methods in space group $C2/c$ using *SHELXLS* (Sheldrick, 2008). Anisotropic displacement parameters and occupancies were refined. The crystal structure of tangdanite was refined to $R_1 [F^2 > 4\sigma(F^2)] = 0.11$, $wR_2(F^2) = 0.28$, $\Delta \rho_{\text{max}} (\text{e } \text{\AA}^{-3}) = 3.493$; $\Delta \rho_{\text{min}} (\text{e } \text{\AA}^{-3}) = -2.184$. Atom parameters are given in Table 4 and interatomic distances are given in Table 5.

The tangdanite structure is based upon complex slabs consisting of Cu, As and Ca coordination polyhedra. This is also seen in tyrolite where they are considered to be nanolayers (Krivovichev *et al.*, 2006). The core of the nanolayer is a Cu arsenate substructure consisting of the A and B sublayers (Fig. 3). The B sublayer represents a series of chains of edge-sharing octahedra $[\text{CuO}_3(\text{OH})_3]$ running along $[010]$. The A sublayer shares corners of AsO_4 tetrahedra with those of $[\text{CuO}_5(\text{H}_2\text{O})]$ octahedra. Outer sides of the layers are filled by Ca octahedra. H_2O molecules and SO_4 groups are situated in the interlayer space. Large values of anisotropic

displacement parameters for interlayer O18, O19 and O20 indicate that the sites O18, O19 and O20 are split. For charge balance maintained in the whole structure, the S site content is 0.5 and we suppose that the sites O18, O19 and O20 may also contain water molecules.

Bond-valence analysis of the structure was performed using *Bond_Str* software (JRC-LLB, version: March 2005) with bond-valence parameters taken from Brese and O'Keeffe (1991). The bond-valence sums obtained are listed in Table 6. Note that the bond-valence sum obtained for the S site is rather small. It has a low occupancy (0.26) and some is replaced by H_2O molecules.

The structure of tangdanite is very similar to that of tyrolite-2M but differs in the interlayer structure. The interlayer structures have been resolved in tangdanite. The interlayer components are the tetrahedral SO_4 ions, but partial substitution of SO_4 for $(\text{H}_2\text{O})_4$ is observed. The SO_4 and $(\text{H}_2\text{O})_4$ tetrahedra have different sizes and this is the most probable cause of the site splitting for O atoms. Due to this splitting there are large U^{ij} values for O19 and O20. The same is seen in tyrolite-1M; in the tyrolite-2M interlayer, the

TABLE 5. Interatomic distances ($\text{\AA}$) in tangdanite.

Cu1–O14 ⁱ	2.349(17)	Cu4–O14 ⁱ	1.987(16)
Cu1–O13 ⁱⁱ	2.357(17)	Cu4–O9	2.032(16)
Cu1–O16	2.396(20)	Cu4–O12	2.241(19)
Cu1–O17	2.416(22)	Cu4–O10	2.850(40)
Cu1–O18	2.424(31)	Cu5–O11	1.927(15)
Cu1–O15	2.469(17)	Cu5–O9	1.959(14)
Cu1–O12	2.655(17)	Cu5–O13 ⁱⁱ	2.017(16)
Cu1–O2 $\times 2$	1.904(16)	Cu5–O6 ^{iv}	2.033(16)
Cu1–O1 $\times 2$	2.031(15)	Cu5–O12	2.227(17)
Cu1–O3 $\times 2$	2.597(16)	Cu5–O10	2.438(39)
Cu2–O5 ^{iv}	1.918(15)		
Cu2–O2	1.928(16)	As1–O4	1.684(17)
Cu2–O3	1.975(16)	As1–O5	1.688(17)
Cu2–O1	2.087(16)	As1–O7	1.689(18)
Cu2–O2 ^v	2.339(17)	As1–O6	1.707(15)
Cu2–O8	2.610(40)	As2–O13	1.676(17)
Cu3–O3	1.932(16)	As2–O12	1.677(18)
Cu3–O9	1.962(16)	As2–O15	1.694(16)
Cu3–O4	1.973(17)	As2–O14	1.740(14)
Cu3–O6 ^{iv}	1.978(16)		
Cu3–O7 ^{vi}	2.418(17)	S1–O19	1.599(99)
Cu3–O8	2.450(40)	S1–O18	1.456(52)
Cu4–O11 ⁱ	1.938(16)	S1–O20 ^{vii}	1.604(102)
Cu4–O7 ^{vi}	1.978(16)	S1–O20	1.683(106)

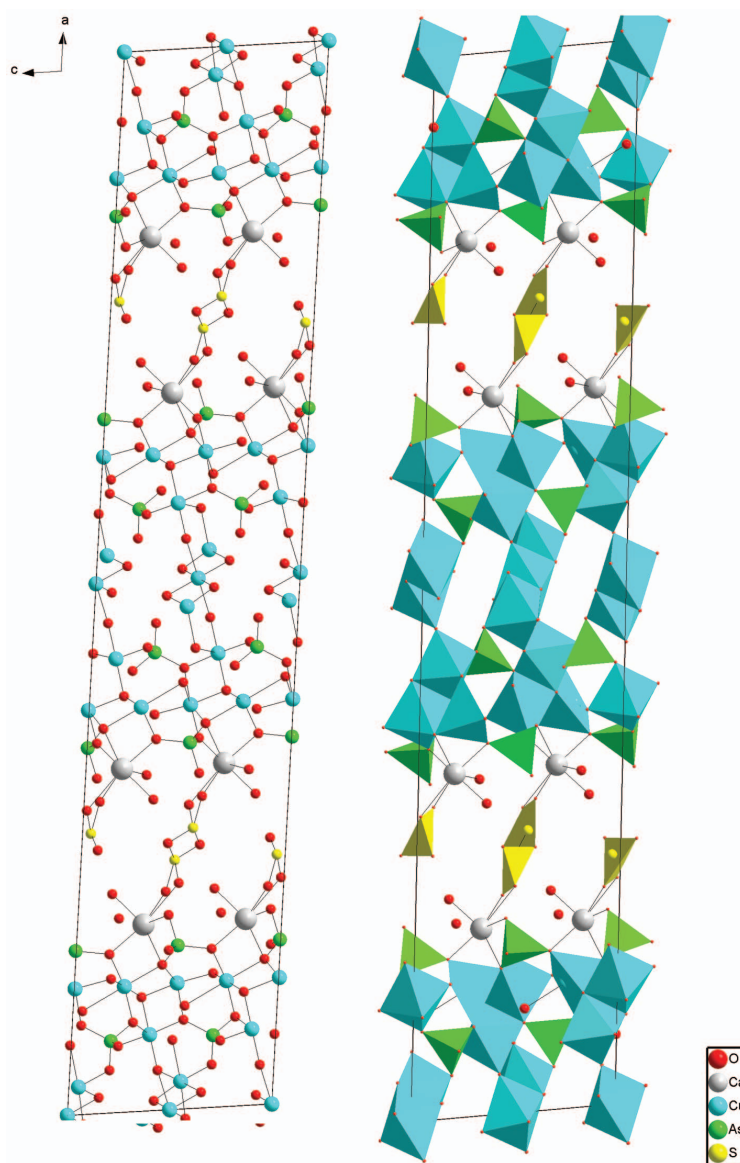


FIG. 3. Crystal structure of tangdanite: general view.

components are CO_3 groups. The interlayer contains ~50% occupancy by carbonate groups attached to the O7 site, but is significantly disordered (Krivovichev *et al.*, 2006).

Infrared spectroscopy

Infrared absorption spectra of tangdanite (holotype sample) and tyrolite from the Beryozovsk

gold deposit, Middle Urals, Russia have been obtained for powdered samples (mixed with anhydrous KBr and pelletized) using a SPECORD 75 IR spectrophotometer. A pure KBr disk was used as a reference. The chemical composition of tyrolite is (by electron microprobe data, in wt.%): Al_2O_3 2.32, P_2O_5 0.91, SO_3 below detection limit of 0.1, CaO 6.62, CuO 47.57, As_2O_5 27.81, total 85.23 ignoring water, which

TABLE 6. Bond-valence sums for atoms in the structure of tangdanite.

Atom	Occupancy	BVSum	Site assignment
Ca1		2.02(4)	Ca
Cu1		1.86(4)	Cu
Cu2		1.98(40)	Cu
Cu3		2.08(4)	Cu
Cu4		1.98(4)	Cu
Cu5		2.08(4)	Cu
As1		4.90(11)	As
As2		4.85(11)	As
S1	0.26	3.74(42)	S
O1		0.72(2)	OH
O2		1.22(3)	OH
O3		0.95(3)	OH
O4		1.70(6)	O
O5		1.76(6)	O
O6		2.01(5)	O
O7		1.82(6)	O
O8	0.57	0.12(1)	H ₂ O
O9		1.32(3)	O
O10	0.67	0.13(1)	H ₂ O
O11		1.01(3)	OH
O12		1.88(6)	O
O13		2.03(6)	O
O14		1.87(5)	O
O15		1.48(5)	O
O16		0.31(2)	H ₂ O
O17		0.30(2)	H ₂ O
O18		0.70(6)	H ₂ O
O20	0.49	0.50(10)	O,H ₂ O
O19	0.86	0.28(7)	O,H ₂ O

corresponds to the empirical formula $\text{Ca}_{0.93}(\text{Cu}_{4.71}\text{Al}_{0.36})[(\text{AsO}_4)_{1.90}(\text{PO}_4)_{0.10}](\text{CO}_3)_x(\text{OH})_y \cdot n\text{H}_2\text{O}$.

Infrared spectra (Fig. 4) of tyrolite and tangdanite in the region of the As–O stretching vibrations ($800\text{--}900\text{ cm}^{-1}$) are similar. However, the main

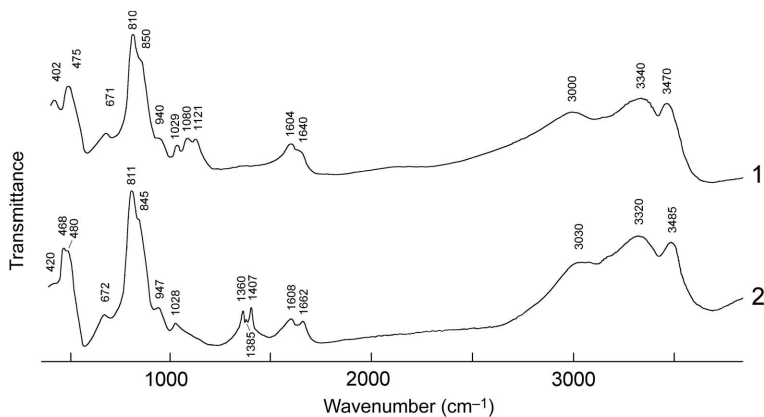


FIG. 4. Infrared spectra of tangdanite (curve 1) and tyrolite (curve 2).

TABLE 7. Comparative data for tangdanite and some related monoclinic Cu arsenates.

	Tangdanite	Tyrolite-1M	Tyrolite-2M	Ruffite	Strashimirite	Leogangite
Chemical formula	$\text{Ca}_2\text{Cu}_9(\text{AsO}_4)_4(\text{SO}_4)_{0.5}(\text{OH})_9 \cdot 9\text{H}_2\text{O}$	$[\text{Ca}_2\text{Cu}_9(\text{AsO}_4)_4(\text{OH})_8(\text{CO}_3)(\text{H}_2\text{O})_{11}](\text{H}_2\text{O})_x$	$\text{Ca}_2\text{Cu}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$	$\text{Cu}_8(\text{AsO}_4)_4(\text{OH})_4 \cdot 5\text{H}_2\text{O}$	$\text{Cu}_{10}(\text{AsO}_4)_4(\text{SO}_4)(\text{OH})_6 \cdot 8\text{H}_2\text{O}$	
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/m, P2$ or Pm	$C2/c$
Unit-cell parameters	a 54.4902 Å b 5.5685 Å c 10.4690 Å β 96.29(0)° V 3157.44 Å ³ $Z = 4$	a 27.562 b 5.5682 c 10.466 β 98.074° V 1590.3 $Z = 4$	a 54.520 b 5.564 c 10.465 β 96.432° V 3154.4 $Z = 4$	a 5.8618 b 12.7854 c 5.7025 β 109.425° V 403.05 $Z = 2$	a 9.71 b 18.81 c 8.94 β 97.2° V 1619.97 $Z = 6$	a 21.77 b 12.327 c 10.72 β 92.85° V 2873.53 $Z = 4$
Strongest powder lines	I d_{meas} 100 4.7815 71 4.3331 54 5.263 47 3.9492 46 2.9763 41 2.6306 29 2.3683 24 1.7439 20 3.3503 20 1.6441	I d_{meas} 100 28.0 80 14.1 30 5.60 40 5.27 70 4.85 50 4.44 70 2.98 70 2.69	I d_{meas} 100 2.827 92 3.377 89 2.983 59 4.177 56 3.190 49 2.114 42 5.087 41 3.800	I d_{meas} 100 18.74 100 2.86 80 9.46 90 8.97 90 3.13 80 4.79 80 4.21 80 3.35	I d_{meas} 100 10.85 20 10.70 10 5.51 10 5.44 10 3.85 10 3.625 10 3.09 10 2.605	I d_{meas} 100 10.850 50 5.4400 30 4.900 30 3.7280 50 3.6250 40 3.0900 40 2.6720 60 2.6300 60 2.6300
Optical data	Biaxial(−) α 1.666 β 1.686 γ 1.694 $2V = 64^\circ$	Biaxial(−) α 1.694 β 1.726 γ 1.730 $2V = 36^\circ$	Biaxial(−) α 1.725 β 1.734 γ 1.740 $2V = 78^\circ$	Biaxial(−) α 1.726 γ 1.747 $2V = 70^\circ$	Biaxial(−) α 1.59 β 1.740 γ 1.744 $2V = 18^\circ$	Biaxial(−) α 1.590 β 1.740 γ 1.744 $2V = 18^\circ$
Hardness	2–2½	1½–2	3	2½–3	NA	NA
Density	3.22 g cm ^{−3}	3.32	3.77	3.76	3.55	3.545
Reference	this work	Ma <i>et al.</i> (1980); Krivovichev <i>et al.</i> (2006)	Yang <i>et al.</i> (2011)	Mincheva-Stefanova (1968)	Lengauer <i>et al.</i> (2004)	Mandarino (2004)

differences between these minerals lies in the SO_4^{2-} bands at 1080 and 1121 cm^{-1} , corresponding to degenerate stretching of SO_4^{2-} (asymmetric S–O vibrations) in tangdanite and CO_3^{2-} (bands at 1360, 1385 and 1407 cm^{-1}) in tyrolite. Other bands of carbonate groups (in the ranges 700–900 and 1000–1100 cm^{-1}) are too weak to be observed at the scale of Fig. 2. Note that the bands of symmetric stretching vibrations of CO_3^{2-} groups (in the range 1000–1100 cm^{-1}) can be present in the IR absorption spectra only when the CO_3 ion is distorted. There are also minor differences in H bonding of H_2O molecules (3000–3500 cm^{-1} , O–H-stretching vibrations; 1600–1700 cm^{-1} , bending vibrations; 400–700 cm^{-1} , mixed modes involving libration vibrations of H_2O). In the IR spectrum of tyrolite, bands of asymmetric S–O stretching vibrations are absent; the band at 1028–1029 cm^{-1} corresponds, in all probability, to stretching vibrations of a PO_4^{3-} impurity. However, one cannot exclude the possibility that in tangdanite the band at 1029 cm^{-1} is related to symmetric stretching vibrations of SO_4^{2-} (non-degenerate mode). In IR spectra of some sulfate minerals with distorted SO_4 tetrahedra (e.g. alunite, this work) a relatively strong band can be present in the range 980–1035 cm^{-1} .

Conclusions

Tangdanite is structurally closely related to, but is not identical to, tyrolite. It is chemically related to leogangite (Table 7). Krivovichev *et al.* (2006) postulated that it is the tyrolite-1M polytype. However, they indicated that they were unable to examine the type material or a specimen from the type locality, which Ma *et al.* (1980) and Liao *et al.* (1996) reported to be S-rich and carbonate-deficient, as well as belonging to a different crystallographic class. Although Krivovichev *et al.* (2006) reported that all tyrolite samples are monoclinic, they never established that ‘clinotyrolite’ is in fact tyrolite. They also indicated that the CO_3^{2-} ion in tyrolite is a species-defining interlayer component occupying its own site in the structure (i.e. it does not substitute for AsO_4^{3-}). The structural formula of tyrolite can be written as $[\text{Ca}_2\text{Cu}_9(\text{AsO}_4)_4(\text{OH})_8(\text{CO}_3)(\text{H}_2\text{O})_{11}](\text{H}_2\text{O})_x$ where $x = 0$ to 1. The formerly named ‘clinotyrolite’ does not contain CO_3^{2-} groups at all and hence it is obviously a separate mineral species.

In this re-examination, previously determined data (Ma *et al.*, 1980; Liao *et al.*, 1996) have been

largely confirmed and have been further refined, although density could not be remeasured. As stated above, CO_2 is a determinative, species-defining constituent of tyrolite. Tangdanite was shown through IR analysis to be completely devoid of CO_2 . Furthermore, chemical analysis shows that S is significant for this mineral’s structure, which is not the case for tyrolite. The structure of tangdanite, while similar in some aspects to tyrolite, is very different in interlayer composition and structure. This study has reconfirmed distinct differences between tangdanite, tyrolite and other minerals and has shown tangdanite to be unique.

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