

Jacquedietrichite, $\text{Cu}_2[\text{BO}(\text{OH})_2](\text{OH})_3$, a new mineral from the Tachgagalt mine, Morocco: Description and crystal structure

ANTHONY R. KAMPF^{1,*} & GEORGES FAVREAU^{2,**}

¹Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard,
Los Angeles, CA 90007, USA

²421 Avenue Jean Monnet, 13090 Aix-en-Provence, France

Abstract: Jacquedietrichite, $\text{Cu}_2[\text{BO}(\text{OH})_2](\text{OH})_3$, space group *Pnma*, $a = 9.455(2)$, $b = 5.866(2)$, $c = 8.668(2)$ Å, $V = 480.8$ Å³, $Z = 4$, is a new mineral from the Tachgagalt mine, Morocco. The strongest eight lines of the X-ray powder-diffraction pattern [d in Å (I) (hkl)] are: 4.734 (100) (200), 3.941 (90) (102), 3.192 (40) (202), 2.545 (45) (302), 2.489 (50) (220), 1.922 (50) (322), 1.838 (40) (420), 1.712 (40) (124). It occurs as transparent bright-blue blades, sometimes intergrown into broader tablets, and as aggregates of pale-blue scales. It is found in small cavities in gaudefroyite-calcite rock and as inclusions in calcite. Blades do not exceed 0.5 mm in length and 0.02 mm in thickness (parallel to {001}), and often taper somewhat in thickness from tip to base. The forms in order of prominence are {001}, {100} and {010}. The streak is pale blue, the luster is vitreous and the hardness is about 2. Blades are slightly flexible with irregular fracture and exhibit a perfect and very easy {100} cleavage and good {010} and {001} cleavages. The measured density (by sink-float) is 3.28(5) g/cm³; the calculated density is 3.303 g/cm³. The mineral dissolves quickly in dilute HCl. Electron microprobe analyses yielded CuO 72.68, CaO 0.11, SiO₂ 1.00, B₂O₃ (calc.) [14.57], H₂O (calc.) [18.85], total 107.21 wt%. CaO and SiO₂ are considered to be from impurities and the high total to be due to volatilization. Jacquedietrichite is biaxial (-) with $\alpha = 1.627(2)$, $\beta = 1.699(2)$, $\gamma = 1.769(2)$, $2V$ (calc.) = 86°, strong pleochroism: X (deep blue) > Y (medium blue) > Z (pale blue); orientation: X = *a*, Y = *c*, Z = *b*. The name honors Jacques Emile Dietrich, Ph.D., of Nice, France (born 1926), retired geologist/mineralogist (Chief Geologist - Autonomous Corps of Geologists of Overseas French Territories) who worked extensively in Morocco. Dr. Dietrich discovered the new mineral. The crystal structure of jacquedietrichite was solved by direct methods and refined by full-matrix least-squares techniques to $R = 6.57\%$ for 295 observed reflections [$F_o > 4\sigma(F_o)$]. Difference maps allowed the approximate location of all hydrogens. CuO₆ octahedra form *trans* edge-sharing (rutile-like) chains parallel to [010]. The CuO₆ octahedra exhibit typical Jahn-Teller distortion with lengthened Cu-O bonds corresponding to the *trans* apical vertices that do not participate in the octahedral edge-sharing. The octahedral chains are joined into layers parallel to (100) by sharing the apical octahedral vertices in the [001] direction. Triangular BO(OH)₂ groups link the octahedral layers in the [100] direction yielding a framework structure. Jacquedietrichite is the only known mineral containing the BO(OH)₂ group and its structure is not closely related to any other known borate mineral. In the structural hierarchy of copper-oxysalt minerals, jacquedietrichite has an M=M-T framework structure, but the structure is not topologically similar to that of any known copper-oxysalt mineral.

Key-words: jacquedietrichite, new mineral, crystal structure, copper, borate, Tachgagalt (Morocco).

Introduction

In the early 1960's Pascal Gallo, chief miner at the manganese mine at Tachgagalt (17 miles south of Ouarzazate, Anti-Atlas Mountains, Morocco) noticed an association of unusual minerals in Vein #2. He presented a specimen of the material to Georges Jouravsky, chief geologist, Division de la Géologie du Maroc, who in turn passed it along to French mineralogist Abbé Christophe Gaudefroy. Marokite was the first new mineral to be described from this association (Gaudefroy *et al.*, 1963)

and subsequently the new minerals gaudefroyite (Jouravsky and Permingeat, 1964), jouravskite (Gaudefroy & Permingeat, 1965), despujolsite (Gaudefroy *et al.*, 1968), henritermierite (Gaudefroy *et al.*, 1969) and neltnerite (Baudracco-Gritti *et al.*, 1982) were described.

On a visit to the mine in 1967, French geologist/mineralogist Jacques Emile Dietrich (Fig. 1) collected specimens from the aforementioned area of the mine. Dr. Dietrich brought these specimens back to France in two wooden boxes, which were then stored in a warehouse. In 1999 or 2000 Dr. Dietrich finally opened the boxes and showed the

*Email: akampf@nhm.org *Email: favreaug@aol.com

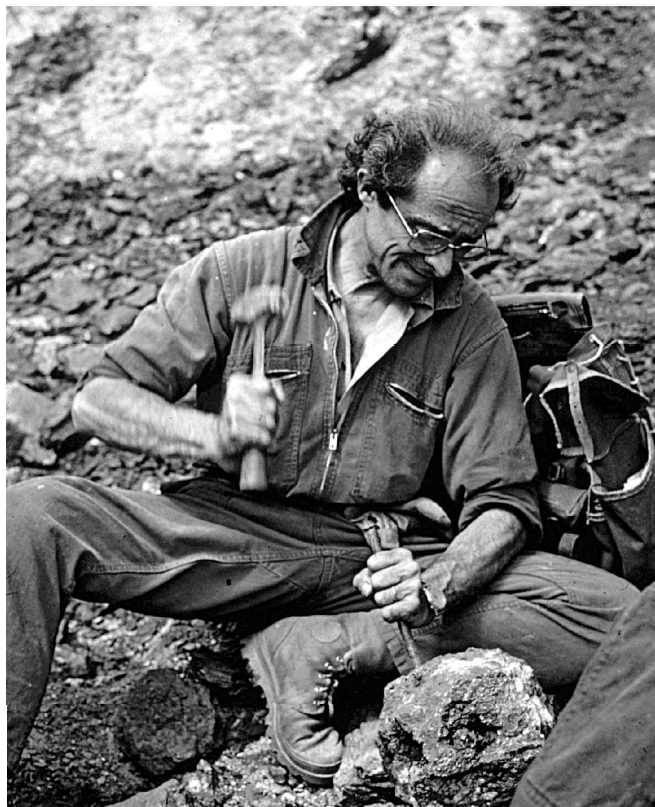


Fig. 1. Jacques Emile Dietrich collecting in the Saint Pons area, Alpes de Haute Provence, France, in 1976. Photo by Louis Steve.

specimens to one of the authors (GF) who noticed the blue crystals that are herein described as a new mineral species.

The new mineral is named for Jacques Emile Dietrich, Ph.D., of Nice, France (born 1926), retired geologist/mineralogist. Dr. Dietrich's professional career began in 1949, first in Morocco, then Madagascar, French West Africa, Morocco again (1960-1967), and finally in France. His last professional title was "Géologue en Chef du Corps Autonome des géologues de la France d'Outre-Mer" (Chief Geologist - Autonomous corps of geologists of Overseas French Territories).

The holotype specimen is housed in the mineral collection of the Natural History Museum of Los Angeles County (catalog number 52461).

Occurrence

The Tachgagalt deposit belongs to a large group of manganese deposits in the Anti-Atlas region, and especially to a group of deposits in the Ouarzazate district, linked to andesitic and rhyo-ignimbritic volcanic activity of Pre-Cambrian III age (or lower Infra-Cambrian). The Tachgagalt deposit is comprised of three roughly parallel veins striking approximately NNE-SSW. Vein #2 (Fig. 2), which dips 80° W, is bounded by ignimbrites and rhyolites. Its main width varies between 1 and 2.5 m and it was noted to extend over 200 m in length and 30 m in depth. The vein rock shows a characteristic banded structure, with hematite at one face and hematite-rich dolomite with some quartz at the other.

The paragenesis of the rare minerals of Vein #2 never could be studied in place. It occurred in a side area of the vein, which was mined before the discovery of the first new species in 1962. Such minerals were never found in the other veins of Tachgagalt. In 1964 an unsuccessful attempt was made to find a possible continuation of this rare mineralization. The conclusion was that the assemblage had been totally mined out.

Jacquedietrichite from Vein #2 occurs in gaufroyite-calcite rock in small cavities and as inclusions in calcite. Associated minerals are gaufroyite, calcite and henritermierite. The mineral probably formed as a secondary low-temperature product of hydrothermal reworking of boron-bearing manganese-oxide ore (gaufroyite).

Physical and optical properties

Jacquedietrichite occurs as bright-blue blades, sometimes intergrown into broader tablets, and as aggregates of powder-blue scales. The crystal form {001} is dominant and blades are bounded by {100} and {010}. No twinning was noted. Blades do not exceed 0.5 mm in length and 0.02 mm in thickness (parallel to {001}), and often taper somewhat in thickness from tip to base (Fig. 3).

The streak of jacquedietrichite is pale blue. Crystals exhibit vitreous lustre. The mineral is non-fluorescent. The hardness could not be accurately measured, but the mineral is very soft, probably having a Mohs hardness less than 2. Crystals are slightly flexible and exhibit perfect and very



Fig. 2. Tachgagalt mine. Vein #2 is seen as the dark gash in the hill at the center of the photograph. Composite of three photographs taken by Jacques Emile Dietrich in 1967.

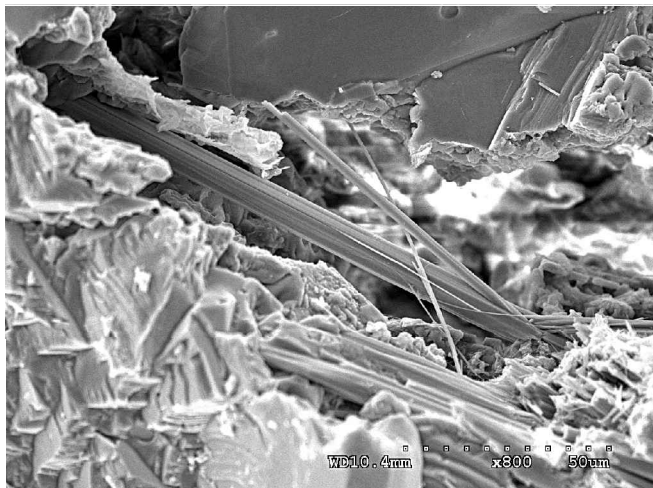


Fig. 3. SEM image of jacquesdietrichite.

easy cleavage on {010} and good cleavage on {100} and {001}. Fracture is uneven. The mineral dissolves quickly in dilute HCl. The specific gravity measured by sink-float in Clerici solution is 3.28(5) g/cm³. The calculated density based on the ideal composition is 3.303 g/cm³.

Crystals are optically biaxial (-). Indices of refraction measured in white light are α 1.627(2), β 1.699(2), γ 1.769(2). The 2V angle could not be determined, but clearly is very large; the calculated 2V is 86°. No dispersion was observed. The optical orientation is X = a, Y = c, Z = b. Pleochroism is very pronounced: X (deep blue) > Y (medium blue) > Z (pale blue).

Chemistry

Chemical analyses of jacquesdietrichite were performed by electron microprobe (WDS mode, 15 kV, 25 nA, beam diameter ~ 5 μ m). The results of eight analyses and corresponding atomic proportions are reported in Table 1. Boron was qualitatively detected using the light-element spectrometer of the microprobe, but nothing approaching quantitation was possible because of the rough surface of the sample.

The very small amount of material available precluded the determination of H₂O and B₂O₃ by direct measurement using other methods. The amounts noted in Table 1 were calculated by stoichiometry from the results of the crystal-structure analysis.

The small amounts of CaO and SiO₂ are interpreted as impurities attributable to very small scale inclusions because Ca and Si do not appear to be accommodated in the jacquesdietrichite structure. Unfortunately, because jacquesdietrichite crystals do not take a good polish, it was not possible to directly observe and thereby confirm the presence of such inclusions.

Discounting SiO₂ and CaO, the only analyzed component is CuO. The high values for CuO in the analyses (and the high total) are attributed to the rough sample surface and significant devolatilization encountered during the

Table 1. Electron Microprobe analysis of jacquesdietrichite.

Constituent	Wt.%	Range	Std. Dev.	Probe Standard
CuO	72.68	68.63-77.00	2.39	Cu metal
CaO	0.11	0.07-0.17	0.03	Synthetic diopside
SiO ₂	1.00	0.61-2.83	0.39	Synthetic diopside
B ₂ O ₃	14.57*			
H ₂ O	18.85*			
Total	107.21			

* Based on ideal formula from crystal structure

probe analyses. The wt.% CuO must be factored down accordingly and, because the only analyzed component is CuO, no empirical formula is provided. The simplified formula is Cu₂[BO(OH)₂](OH)₃.

The cell parameters and details of the structure analysis showed jacquesdietrichite to be identical to synthetic Cu₂[BO(OH)₂](OH)₃. Behm & Baerlocher (1985) determined the atomic structure of this compound by Reitveld analysis and reported a complete wet-chemical analysis (Table 2).

The Gladstone-Dale compatibility index [$1 - (K_p/K_C)$] is -0.014 (superior), based on the ideal formula and calculated density and -0.020 (excellent), based on the ideal formula and measured density.

X-ray crystallography and structure data collection

X-ray powder-diffraction data (Table 3) were obtained using a Gandolfi camera (114.6 mm diameter, Ni-filtered CuK α radiation). The data show good agreement with the pattern calculated from the structure. The unit-cell data refined from the 3-circle diffractometer data are provided in Table 4 along with the unit-cell data for the synthetic compound reported by Behm & Baerlocher (1985).

Structure data collection was performed on a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD detector. A full sphere of three-dimensional data were collected from a thin tabular crystal fragment of jacquesdietrichite from the type specimen. Fifty duplicate frames acquired at the end of the data collection indicated that no significant decay had taken place. The measured intensities were corrected for Lorentz and polarization effects using the program SAINT and an empirical absorption correction was applied using the program SADABS (Bruker, 1997).

Table 2. Wet chemical analysis of synthetic Cu₂[BO(OH)₂](OH)₃.

Constituent	Wt.%	Method	Theor. Wt.%
CuO	65.6	Electrolysis	66.6
B ₂ O ₃	16.4	Acidimetric	14.6
H ₂ O	19.1	Thermogravimetric	18.8
Total	101.1		100.0

From Behm & Baerlocher (1985)

Table 3. Jacquesdietrichite powder data.

I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl
100	4.734	4.728	93	200
25	4.330	4.334	26	002
90	3.941	3.940	100	102
40	3.192	3.195	45	202
25	2.933	2.933	13	020
30	2.759	2.763	17	103
45	2.545	2.549	33	302
50	2.489	2.492	31	220
5	2.426	2.429	5	022
10	2.394	2.395	8	221
25	2.351	2.353	24	122
15	2.160	2.161	15	222
20	2.109	2.112	18	104
5	2.071	2.075	6	402
50	1.922	1.924	34	322
40	1.838	1.841	20	420
10	1.784	1.786	8	304
40	1.712	1.714	28	124
5	1.692	1.694	11	422
5	1.575	1.576	3	600
5	1.526	1.525	6	324
5	1.491	1.492	9	522
20	1.466	1.467	5	040
10	1.422	1.425	6	504
5	1.400	1.401	4	240
10	1.389	1.388	7	620
10	1.375	1.374	6	142

Structure solution and refinement

The SHELXL97 software (Sheldrick, 1997) was used for the determination and refinement of the structure. The Cu and O atoms were readily located by direct methods. The B position was obvious from a difference-Fourier syntheses. In subsequent refinement cycles, anisotropic displacement parameters for Cu and isotropic displacement parameters for B and O atoms were refined. The R1 (conventional R factor) converged to 6.76 % for 295 reflections with $F_o > 4\sigma(F_o)$. Despite the relatively low quality of the refinement, the difference Fourier showed significant positive electron density in regions consistent with reasonable H atom sites (based upon valence-bond and geometrical considerations). The unconstrained refinement of the

Table 4. Cell data for jacquesdietrichite and synthetic $\text{Cu}_2[\text{BO}(\text{OH})_2](\text{OH})_3$.

	Jacquesdietrichite*	$\text{Cu}_2[\text{BO}(\text{OH})_2](\text{OH})_3$ **
Space group	$Pnma$	$Pnma$
a (Å)	9.455(2)	9.4459(2)
b (Å)	5.866(2)	5.8590(1)
c (Å)	8.668(2)	8.6802(2)
V (Å ³)	480.8(2)	480.4(2)
Z	4	4

* refined from diffractometer data

** from Behm & Baerlocher (1985)

Table 5. Data collection and structure refinement details for jacquesdietrichite.

Diffractometer	Bruker SMART Platform CCD
X-ray radiation / power	MoK α ($\lambda = 0.71073$ Å) / 50 kV, 45 mA
Temperature	298(2) K
Absorption coefficient	8.79 mm ⁻¹
F(000)	464
Crystal size ($\mathbf{a} \times \mathbf{b} \times \mathbf{c}$)	0.025 x 0.130 x 0.012 mm
Frame number / width / time	1271 / 0.3° in ω / 30 sec
θ range	3.19 to 28.26°
Index ranges	-12 $\leq h \leq$ 12, -7 $\leq k \leq$ 7, -11 $\leq l \leq$ 9
Reflections collected	2923
Independent reflections	646 [$R_{\text{int}}^* = 0.0585$]
Reflections, $F_o > 4\sigma(F_o)$	295
Completeness to $\theta = 28.26^\circ$	99.1%
Refinement method	Full-matrix least-squares on F^2
Parameters refined	39
Goof [†]	1.078
R indices [$F_o > 4\sigma(F_o)$]	$R(F)^\ddagger = 6.57\%$, $wR(F^2)^\S = 19.66\%$
R indices (all data)	$R(F) = 13.63\%$, $wR(F^2) = 25.45\%$
Largest diff. peak / hole	+2.18 / -1.48 e/Å ³

* $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$. † $\text{Goof} = S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n-p) \}^{1/2}$. ‡ $R(F) = \sum |F_o| - |F_c| / \sum |F_o|$. § $wR(F^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where a is 0, b is 12.994 and P is $[2F_c^2 + \text{Max}(F_o^2, 0)] / 3$

Table 6. Atomic coordinates and equivalent isotropic displacement parameters for jacquesdietrichite.

Atom	x	y	z	U_{eq}
Cu	0.2489(2)	0.0019(3)	0.9249(2)	0.0113(6)*
B	0.015(2)	0.25	0.172(3)	0.004(4)
O1	0.0897(9)	0.0534(15)	0.1781(10)	0.009(2)
O2	0.3629(13)	0.25	0.0044(15)	0.009(3)
O3	0.3464(13)	0.75	0.0221(16)	0.007(3)
O4	0.3707(14)	0.25	0.3501(15)	0.011(3)
O5	0.3656(13)	0.75	0.3304(15)	0.005(3)
H1	0.018(12)	0.966(24)	0.188(20)	0.05
H2	0.428(19)	0.25	0.072(22)	0.05
H3	0.435(5)	0.75	0.004(31)	0.05
H5	0.384(28)	0.75	0.235(7)	0.05

* Anisotropic displacement parameters for Cu: $U_{11} = 0.0122(9)$, $U_{22} = 0.0039(9)$, $U_{33} = 0.0178(9)$, $U_{23} = 0.0004(7)$, $U_{13} = -0.0053(6)$, $U_{12} = 0.0002(6)$.

Table 7. Selected bond distances (Å) and angles (°) in jacquesdietrichite.

Cu – O3	1.935(8)	B – O1	1.351(13)
Cu – O2	1.938(8)	B – O1	1.351(13)
Cu – O4	1.970(9)	B – O4	1.382(23)
Cu – O5	1.990(9)	<B – O>	1.361
Cu – O1	2.648(9)	O1 – B – O1	117.2(16)
Cu – O1	2.678(9)	O1 – B – O4	121.3(8)
<Cu – O>	2.193	O1 – B – O4	121.3(8)
O1 – O5	2.768(12)	O3 – O2	2.758(2)
O1 – H1	0.85	O3 – H3	0.85
O5 – H1	1.93	O2 – H3	1.91
O1 – H1 – O5	169	O3 – H3 – O2	171
O2 – O4	2.997(17)	O5 – O3	2.678(17)
O2 – H2	0.85	O5 – H5	0.85
O4 – H2	2.47	O3 – H5	1.88
O2 – H2 – O4	121	O5 – H5 – O3	156

Table 8. Bond valence balance for jacquesdietrichite.

	O1	O2	O3	O4	O5	$\Sigma_c v$
	0.073					
Cu	0.067	0.497 x2↓	0.501 x2↓	0.455 x2↓	0.431 x2↓	2.024
B	1.056 x2→			0.971		3.083
H1	0.804				0.196	1.000
H2		0.869		0.131		1.000
H3		0.200	0.800			1.000
H5			0.238		0.762	1.000
$\Sigma_a v$	2.000	2.062	2.039	2.012	1.821	

Cu-O and B-O bond strengths from Brese and O'Keeffe (1991)

H-bond strengths from Ferraris and Ivaldi (1988) based on O...O distances

atomic parameters for these H atom sites yielded generally unacceptable O-H distances; however, with the O-H distances constrained to 0.85 Å and U_{iso} for the H atoms set at 0.05 Å², the refinement was successful and R1 converged slightly to 6.57%. Nevertheless, the low quality of the refinement, the high standard deviations in the H atom coordinates and the large final difference Fourier peaks and holes, +2.18e to -1.48e, indicate that the H atoms cannot be considered well located.

Table 5 gives the details of the data collection and structure refinement, Table 6 the final fractional coordinates and displacement parameters, Table 7 interatomic distances, and Table 8 the bond valences. A listing of the observed and calculated structure factors can be ordered from the authors.

Description of the structure

The structure of jacquesdietrichite, projected along [010] in Fig. 4 and [001] in Fig. 5, is identical with that

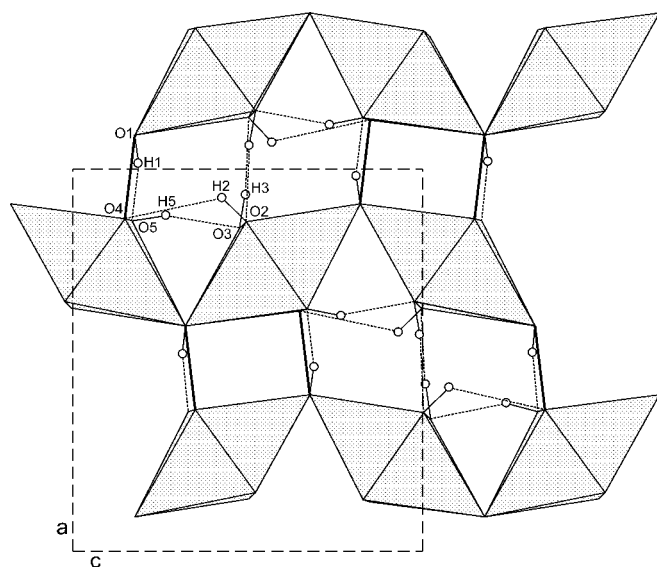


Fig. 4. The structure of jacquesdietrichite viewed along [010]. CuO₆ octahedra are stippled. Triangular BO₃ groups are shown on edge as thick black lines. Circles are H atoms. O-H bonds are shown as thin solid lines. O...H hydrogen bonds are shown as finely dashed lines. The unit cell is outlined by a coarse dashed line.

reported by Behm & Baerlocher (1985) for the synthetic compound, Cu₂[BO(OH)₂](OH)₃. In the structure CuO₆ octahedra form *trans* edge-sharing (rutile-like) chains parallel to [010]. The CuO₆ octahedra exhibit typical Jahn-Teller distortion with lengthened Cu-O1 bonds corresponding to the *trans* apical vertices that do not participate in the octahedral edge-sharing. The octahedral chains are joined into layers parallel to (100) by sharing the apical octahedral vertices in the [001] direction. Triangular BO(OH)₂ groups link the octahedral layers in the [100] direction yielding a framework structure. Hydrogen bonding forms additional chain-to-chain and sheet-to-sheet links.

Relationships to other species

According to the scheme of Hawthorne *et al.* (1996), jacquesdietrichite can be classified as a borate with an insular triangular BΦ₃ group (Φ = O or OH). Sassolite, B(OH)₃, is the only other insular BΦ₃ borate for which

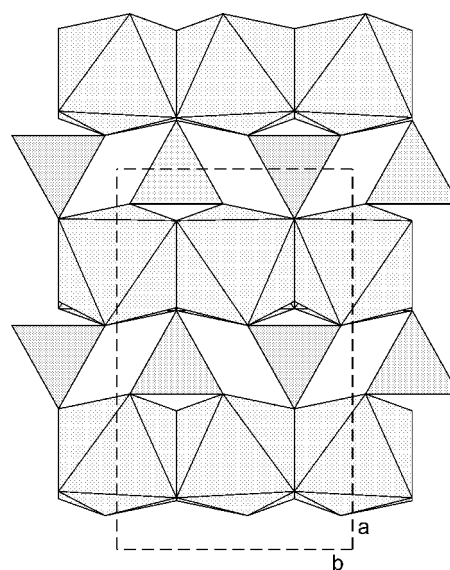


Fig. 5. The structure of jacquesdietrichite viewed along [001]. CuO₆ octahedra are lightly stippled. Triangular BO₃ groups are darkly stippled. H atoms and hydrogen bonds are not shown. The unit cell is outlined by a dashed line.

$\Phi = \text{OH}$, but in jacquesdietrichite only two of the three anions coordinated to B are OH. Jacquesdietrichite is the only known mineral containing the $\text{BO}(\text{OH})_2$ group and its structure is not closely related to that of any other known borate mineral.

In the structural hierarchy of copper-oxysalt minerals presented by Eby and Hawthorne (1993), jacquesdietrichite has an M=M-T framework structure. These structures are characterized by edge-sharing octahedral chains that have a repeat distance of $\sim 3n \text{ \AA}$ (corresponding to $b = 5.866 \text{ \AA}$ in jacquesdietrichite). The edge-sharing chains in these structures are cross-linked by sharing edges and corners with octahedra from other chains, and also by sharing corners with tetrahedra or triangles. Unlike many of the other M=M-T framework structures, the structure of jacquesdietrichite is not a wallpaper structure, in that the structure perpendicular to the length of the chain cannot be represented as a mapping onto a 3^6 net (see also Moore & Araki, 1974).

Furthermore, the structure of jacquesdietrichite is not topologically similar to any of the copper-oxysalt non-wallpaper framework structures. The structure of jacquesdietrichite bears the closest resemblance to that of trippkeite, $\text{Cu}(\text{As}_2\text{O}_4)$. The structure of jacquesdietrichite projected along [001] (Fig. 5) appears quite similar to that of trippkeite projected along [100]. The structure of trippkeite has large channels along [001] (the chain direction). The structure of jacquesdietrichite could be created from that of trippkeite by placing additional edge-sharing octahedral chains in these channels and reorganizing the linkages between the chains and triangular groups.

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