The Canadian Mineralogist
Vol. 34, pp. 73-78 (1996)

THE CRYSTAL STRUCTURE OF CLINOATACAMITE, A NEW POLYMORPH OF $Cu_2(OH)_3Cl$

JOEL D. GRICE

Research Division, Canadian Museum of Nature, P.O. Box 3443, Station "D", Ottawa, Ontario K1P 6P4

JAN T. SZYMAŃSKI

CANMET, Natural Resources Canada, 555 Booth Street, Ottawa, Ontario K1A 0G1

JOHN L. JAMBOR

Department of Earth Sciences, University of Waterloo, Waterloo, Ontario N2L 3G1

ABSTRACT

The crystal structure of clinoatacamite, $Cu_2^{2+}(OH)_3Cl$, has been determined and refined to indices R = 5.2 and wR = 4.9%. The structure is monoclinic, space group $P2_1/n$ (14), with cell parameters a 6.144(1), b 6.805(1), c 9.112(1) Å, β 99.55(3)°, V 375.7(2) Å^3, and with Z = 4. The structure analysis was essential in determining the valence state of copper (Cu^{2+}) and the number of $(OH)^-$ anions in the formula. The structure consists of layers of partly occupied, edge-sharing octahedra of Jahn–Teller-distorted $[Cu(OH)_4Cl_2]$ octahedra parallel to (101). This layer is topologically the same as that in mica. Adjacent layers of octahedra are offset, such that vacant sites in one sheet align with occupied sites in the neighboring sheet. Layers are linked by individual, slightly Jahn–Teller-distorted octahedra of composition $[Cu(OH)_6]$. The structures of paratacamite and the other polymorphs of $Cu_2(OH)_3Cl$, atacamite and botallackite, also are layered, but they differ from the layering of clinoatacamite in topology, composition and cross-linkage.

Keywords: clinoatacamite, crystal structure, layer of octahedra, polymorph, Jahn–Teller distortion.

SOMMAIRE

Nous avons affiné la structure cristalline de la clinoatacamite, $Cu_2^{2+}(OH)_3Cl$, jusqu'à un résidu R de 5.2% (wR = 4.9%). Il s'agit d'une structure monoclinique, groupe spatial $P2_1/n$ (14), dont les paramètres réticulaires sont a 6.144(1), b 6.805(1), c 9.112(1) Å, β 99.55(3)°, V 375.7(2) Å^3, pour Z = 4. L'ébauche de la structure a été essentielle pour fixer la valence du cuivre (Cu^{2+}) et le nombre d'anions OH^- dans la formule chimique. La structure est faite de feuillets parallèles à (101), composés d'octaèdres difformes $[Cu(OH)_4Cl_2]$ partiellement occupés, partageant des arêtes; ces octaèdres sont difformes à cause de l'effet de Jahn–Teller. Ces feuillets sont topologiquement identiques à ceux qui caractérisent les micas. Les feuillets adjacents sont décalés, de sorte que les lacunes d'un feuillet sont alignées avec les sites occupés du feuillet adjacent. Ces feuillets sont liés par des octaèdres individuels de composition $[Cu(OH)_6]$, légèrement difformes, encore à cause de l'effet de Jahn–Teller. Les structures de paratacamite et des polymorphes de $Cu_2(OH)_3Cl$ atacamite et batallackite possèdent aussi ces feuillets; toutefois, elles diffèrent de la structure de la clinoatacamite dans la topologie, la composition et l'interconnexion des feuillets.

(Traduit par la Rédaction)

Mots-clés: clinoatacamite, structure cristalline, feuillet d'octaèdres, polymorphe, distorsion, effet de Jahn–Teller.

INTRODUCTION

Clinoatacamite (monoclinic) from Chuquicamata, Chile, has been described as the third polymorph of $Cu_2^{2+}(OH)_3Cl$ (Jambor *et al.* 1996); atacamite (orthorhombic) and botallackite (monoclinic) are the other polymorphs. Indications are that paratacamite (rhombohedral) is not a fourth polymorph of $Cu_2^{2+}(OH)_3Cl$, as this mineral requires partial substitution of Cu by Zn for stabilization (Jambor *et al.* 1996). The crystal-structure analysis reported here was undertaken in order to understand the crystal-chemical relationships among these four minerals.

EXPERIMENTAL

The small amount of holotype clinoatacamite available precluded standard chemical analytical techniques capable of differentiating the valence state of Cu and the determination of H_2O. The structure-analysis method (Hawthorne & Grice 1990) established these quantities; the formula is $Cu_2^{2+}(OH)_3Cl$. Electron-microprobe analysis (Jambor *et al.* 1996) of the material gave CuO 74.7, Cl 16.5, (H_2O from structure analysis 13.5), sum 104.7, less O ≡ Cl 3.7, total 101.0 wt.%. Zinc and Ni were not detected. Based on O + Cl = 4, the empirical formula is $Cu_{1.96}O_{3.03}H_{3.11}Cl_{0.97}$. The ideal formula, $Cu_2(OH)_3Cl$, requires CuO 74.49, Cl 16.60 and H_2O 12.66, sum 103.75, less O ≡ Cl 3.75, total 100 wt.%. It is evident that within the limits of experimental error, the material studied is ideal, end-member clinoatacamite.

A crystal fragment of type clinoatacamite was used in the collection of X-ray-diffraction intensity data. Single-crystal precession photographs indicate the unique space-group $P2_1/n$ (14), on the basis of systematic absences of reflections. Intensity data were collected on a fully automated CAD four-circle diffractometer operated at 50 kV, 26 mA, with graphite-monochromated Mo*K*α radiation.

A set of 44 reflections was used to orient the crystal and to refine the cell dimensions. Four asymmetric sets of intensity data were collected up to $2\theta = 60°$ using a θ:2θ scan-mode, with scan speeds of approximately 1°/minute. Data pertinent to the collection of the intensity data are given in Table 1.

Data reduction, using the NRCVAX set of computer programs (Gabe *et al.* 1989), included correction for background, scaling, Lorentz and polarization and linear absorption. For the absorption correction, four intense diffraction-maxima in the range 25 to 53° 2θ were chosen for ψ diffraction-vector scans after the method of North *et al.* (1968). Structure determination and structure refinement were done using of the SHELXTL (Sheldrick 1990) package of computer programs. The irregular shape of the crystal precluded a good absorption-correction, and became the limiting factor in the structure refinement. This problem in the data reduction is evidenced by a merging *R* of 12% for the four asymmetric units of reflection data.

CRYSTAL-STRUCTURE ANALYSIS

Normalized structure-factor statistics indicate a centrosymmetric space-group. The *E*-map coordinates were assigned to appropriate scattering curves, three Cu, one Cl and three O atoms. This structure model refined to $R = 6.8\%$.

In the final least-squares refinement, the sites of all atoms were refined with anisotropic displacement-factors to final residuals of $R = 5.2\%$ and $wR = 4.9\%$. The addition of an isotropic extinction-correction did not improve the refinement. Owing to the poor agreement among symmetry-related reflections, $R_{int} = 12.1\%$, the structure was solved and refined in $P1$. This refinement, with isotropic displacement-factors, had a considerably poorer residual factor, with $R = 15.5\%$. The lower-symmetry structure model was tested using MISSYM (Le Page 1987) and found to contain an apparent symmetry of $2_1/m$. This symmetry is consistent with the Cu atomic positions, but the O atoms obey space-group symmetry $P2_1/n$. Refining the structure in $P2_1/m$ with anisotropic displacement-factors results in residual factors $R = 11.3\%$ and $wR = 13.8\%$, and all of the O atoms have non-positive definite displacement-factors. Thus it is evident that $P2_1/n$ is the correct space-group and that the rather poor refinement is attributable to the problems inherent in an absorption correction of an elongate crystal fragment. In the final ΔF-synthesis, residual electron densities of 2 $e^-/Å^3$ remained, but none of these could be satisfactorily assigned to H atoms. The final positional and displacement parameters for the clinoatacamite structure in $P2_1/n$ are given in Table 2, and selected bond-lengths and angles, in Table 3. Observed and calculated structure-factors and anisotropic displacement-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

TABLE 1. CLINOATACAMITE: STRUCTURE-DETERMINATION DATA

Ideal formula:	$Cu_2(OH)_3Cl$	$a = 6.144(1)$ Å
Space group:	$P2_1/n$	$b = 6.805(1)$ Å
Crystal size:	0.14 x 0.06 x 0.04 mm	$c = 9.112(2)$ Å
		$\beta = 99.55(3)°$
Rad./Mon.:	Mo/graphite	$V = 375.7(2)$ Å^3
μ	11.9 mm^{-1}	$Z = 4$
		Total refl. 4186
Min. transmission	0.637	*F* unique 1092
Max. transmission	0.831	$Fo > 6\sigma(F)$ 674
		Final $R = 5.2\%$
$wR = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2]^{1/2}$,	$w = [\delta^2(F_o)]^{-1}$	Final $wR = 4.9\%$

TABLE 2. CLINOATACAMITE: ATOMIC COORDINATES, ISOTROPIC DISPLACEMENT FACTORS AND BOND-VALENCE SUM

Atom	*x*	*y*	*z*	U(Å^2) x 10^2	BVS[1]
Cu1	0	1/2	1/2	1.44(4)	1.98
Cu2	0	0	0	1.68(4)	2.09
Cu3	0.2586(2)	0.2384(1)	0.7485(2)	1.55(3)	2.02
O1	0.2998(10)	0.2962(10)	0.5470(8)	2.2(2)	1.18
O2	0.4190(8)	-0.0141(8)	0.7727(8)	2.2(2)	1.24
O3	0.2596(8)	0.6792(8)	0.5372(8)	1.9(2)	1.27
Cl	0.1116(3)	-0.0038(3)	0.3068(2)	1.87(5)	0.37

[1] Bond-valence sums (*v.u.*) using the parameters of Brese & O'Keeffe (1991).

TABLE 3. CLINOATACAMITE: SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)

Cu1 polyhedron		Cu2 polyhedron		Cu3 polyhedron	
Cu1-O1	2.288(6) x 2	Cu2-O1	1.948(7) x 2	Cu3-O1	1.934(8)
Cu1-O2	2.050(7) x 2	Cu2-O3	1.987(6) x 2	Cu3-O2	1.975(5)
Cu1-O3	1.991(5) x 2	Cu2-Cl	2.766(2) x 2	Cu3-O2'	1.999(5)
				Cu3-O3	2.015(7)
O1-Cu1-O2	74.3(2)	O1-Cu2-O3	83.6(2) x 2	Cu3-Cl	2.756(2)
O1-Cu1-O2'	105.7(2)	O1-Cu2-O3'	96.4(2) x 2	Cu3-Cl'	2.804(2)
O1-Cu1-O3	75.1(2)	O1-Cu2-Cl	99.0(2) x 2		
O1-Cu1-O3'	104.9(2)	O1-Cu2-Cl'	81.0(2) x 2	O1-Cu3-O2	98.2(3)
O2-Cu1-O3	78.5(2)	O3-Cu2-Cl	96.4(2) x 2	O1-Cu3-O2'	83.8(3)
O2-Cu1-O3'	101.4(2)	O3-Cu2-Cl'	83.6(2) x 2	O1-Cu3-Cl	100.3(2)
				O1-Cu3-Cl'	80.2(2)
Cl-O1	3,070(7)			O2-Cu3-O3	79.9(3)
Cl-O2	3.090(6)			O2-Cu3-Cl	84.1(1)
Cl-O3	3.042(6)			O2-Cu3-Cl'	100.6(2)
				O2'-Cu3-O3	98.3(3)
				O2'-Cu3-Cl	92.8(2)
				O2'-Cu3-Cl'	82.4(1)
				O3-Cu3-Cl	83.4(2)
				O3-Cu3-Cl'	96.3(2)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The analysis of the structure of clinoatacamite permitted the calculation of bond-valence sums for the various atomic sites. On the basis of the constants of Brese & O'Keeffe (1991), the sums are: Cu1 1.98, Cu2 2.09, Cu3 2.02, Cl 0.37, O1 1.18, O2 1.24 and O3 1.27 *vu*. These calculations allow assignment of the correct valence, Cu^{2+}, to the cation and recognition of O1, O2 and O3 as $(OH)^-$ anions. The resultant simplest formula for clinoatacamite is $Cu_2^{2+}(OH)_3Cl$ with $Z = 4$. The low bond-valence sum of the Cl atom is due to H-bonding. Each Cl atom is H-bonded to all three O atoms at bond distances of 3.04 to 3.09 Å (Table 3). These bond distances are similar to the average O–Cl distance in paratacamite (3.07 Å: Fleet 1975) and botallackite (3.21 Å: Hawthorne 1985).

The crystal structure of clinoatacamite may be described as made of layers of partially occupied, edge-sharing, Jahn–Teller-distorted $[Cu(OH)_4Cl_2]$ octahedra parallel to (101) (Fig. 1a). This layer is topologically the same as that in mica. Adjacent layers of octahedra are offset such that vacant sites in one sheet align with occupied sites in the neighboring sheet. Layers are linked by individual, slightly Jahn–Teller-distorted octahedra of composition $[Cu(OH)_6]$ (Fig. 1b). Eby & Hawthorne (1993) classified this type of copper oxysalt mineral as an infinite framework structure $M = M$, where M denotes octahedrally coordinated cations, and the double hyphen denotes edge sharing.

In addition to clinoatacamite, it has been assumed that there are three other polymorphs of $Cu_2(OH)_3Cl$, and the crystal structure has been solved for each; atacamite (Parise & Hyde 1986), paratacamite (Fleet 1975) and botallackite (Hawthorne 1985). Like clinoatacamite, each of these structures has layers of octahedra but of differing composition or topology. Botallackite has a layer of fully occupied octahedra, with composition $[Cu(OH)_4Cl_2]$ (Fig. 2a). Adjacent layers are H-bonded together through hydroxyl donors and Cl acceptors (Fig. 2b). In atacamite, the layers of octahedra, and their stacking, resemble those of clinoatacamite, but the vacant sites in the layer correspond to a more distorted "octagonal" hole (Fig. 3). The difference in topology between the layers of clinoatacamite and those in atacamite results from a change in composition within the layer. In clinoatacamite, both octahedra have the composition $[Cu(OH)_4Cl_2]$, whereas in atacamite, the two octahedra have the composition $[Cu(OH)_4Cl_2]$ and $[Cu(OH)_5Cl_1]$. The $[Cu(OH)_4Cl_2]$ octahedron in each structure is (4 + 2)-distorted, with the Cu–Cl bonds being longer than the Cu–O bonds; in atacamite, however, the $[Cu(OH)_4Cl_2]$ octahedron is (4 + 2)-distorted with two apical Cl ligands, and the $[Cu(OH)_5Cl_1]$ octahedron is (4 + 2)-distorted with one apical Cl and one apical O ligand. Paratacamite has the same layer composition and topology as clinoatacamite (Fig. 4a). It is the interlayer, isolated $[Cu(OH)_6]$ octahedron that differs in the two minerals. In the clinoatacamite structure, the interlayer octahedron exhibits a Jahn–Teller distortion, but in paratacamite, one $[Cu(OH)_6]$ is axially compressed whereas the other is a regular octahedron

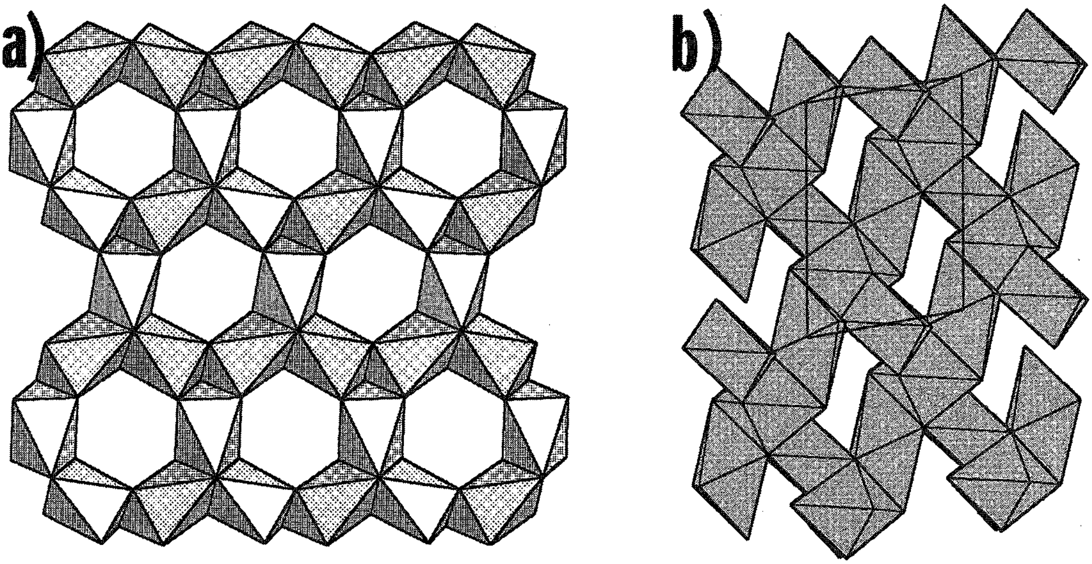

FIG. 1. The structure of clinoatacamite: (a) (101) projection showing the layer of edge-sharing $Cu(OH)_4Cl_2$ octahedra; (b) (010) projection showing (101) layers of $Cu(OH)_4Cl_2$ octahedra with single $Cu(OH)_6$ octahedra cross-linking layers. The unit cell $a < c$ is outlined.

(Fig. 4b). Eby & Hawthorne (1993) remarked on this anomalous occurrence of symmetrically bonded Cu. That paratacamite contains essential Zn (or another cation, *e.g.*, Ni) is strongly suggested by the fact that all paratacamite crystals studied to date contain significant amounts of Zn or Ni (>2 wt.%), even those from the type locality (Jambor *et al.* 1996). Zinc in a 6-fold coordination atomic site usually has fairly regular octahedral coordination. Apparently, the crystal used in the structure determination (Fleet 1975) was not analyzed, and it is probable that the structure does not correspond to a "pure" Cu-bearing compound.

The indications are that paratacamite needs to be redefined, as it is probably not a polymorph of $Cu_4(OH)_6Cl_2$, but a distinct phase of composition $Cu_3(Cu,Zn)(OH)_6Cl_2$. In such a case, the "parata-

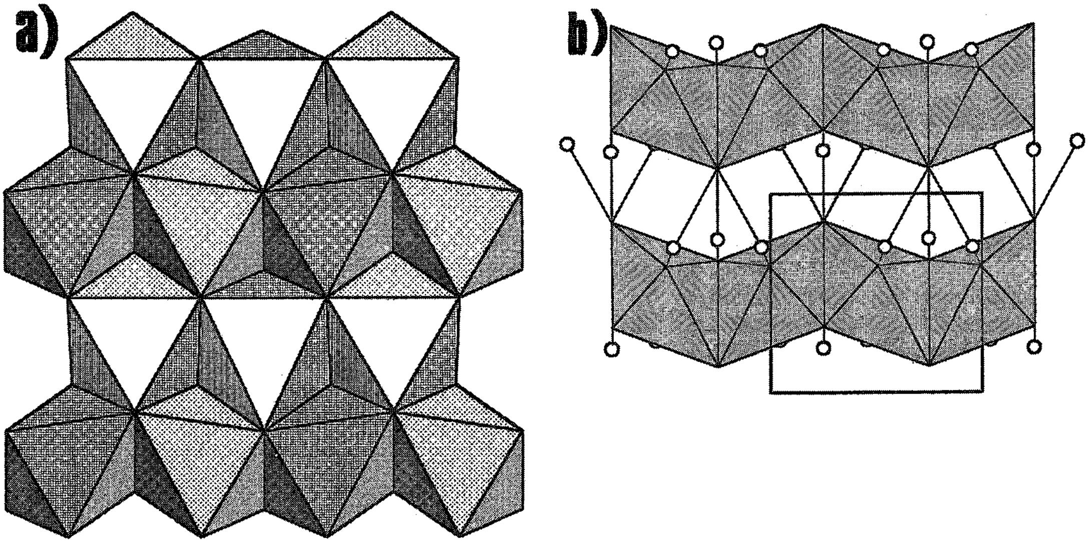

FIG. 2. The structure of botallackite: (a) [100] projection showing a layer of fully occupied edge-sharing octahedra. (b) [001] projection showing (100) layering of $Cu(OH)_4Cl_2$ octahedra and H-bonding linking layers. The unit cell $a < b$ is outlined.

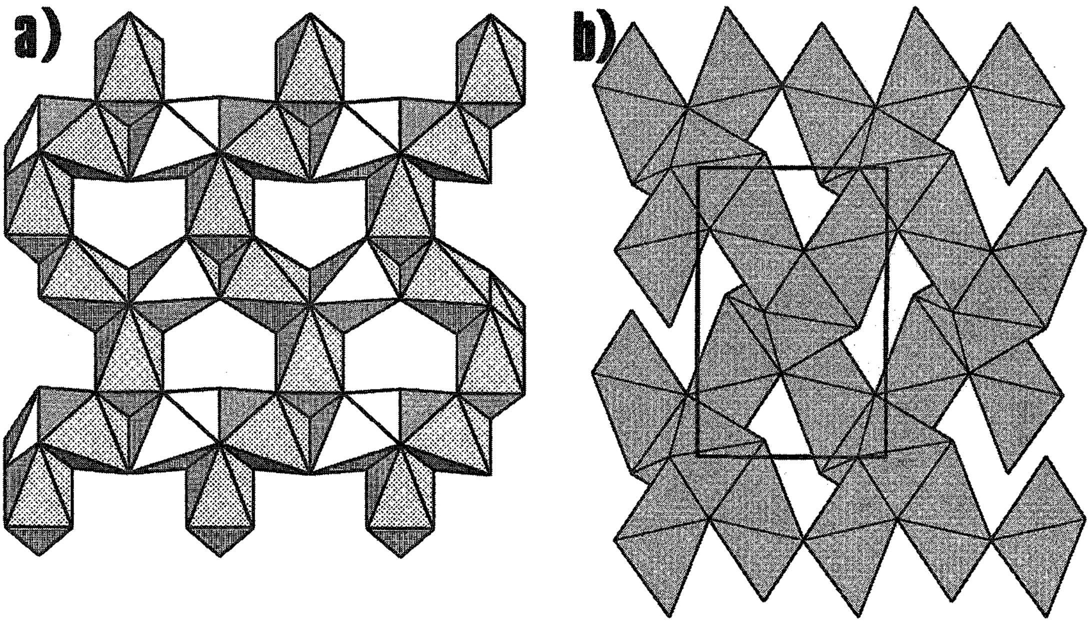

FIG. 3. The structure of atacamite: (a) (110) projection showing the layer of edge-sharing $Cu(OH)_4Cl_2$ octahedra; (b) (001) projection showing (110) layering of $Cu(OH)_4Cl_2$ octahedra with single $Cu(OH)_5Cl_1$ octahedra cross-linking layers. The unit cell $a < b$ is outlined.

camite" structure would have Zn ordered at the regular octahedral site within equipoint position 3*b*. Jambor *et al.* (1996) showed that only 2 wt.% Zn was necessary to stabilize the rhombohedral (paratacamite) structure; thus Zn need not be the dominant cation in the 3*b* site. Such a redefinition requires approval by the Commission on New Minerals and Mineral Names, IMA. It would be appropriate that rhombohedral $Cu_3(Cu,Zn)(OH)_6Cl_2$, with *a* 13.65 and *c* 14.0 Å, space group $R\bar{3}$, which corresponds to the holotype from Sierra Gorda, Chile, and for which the crystal structure was determined by Fleet (1975), be retained to designate the mineral paratacamite. If paratacamite is redefined in this way, the following may be con-

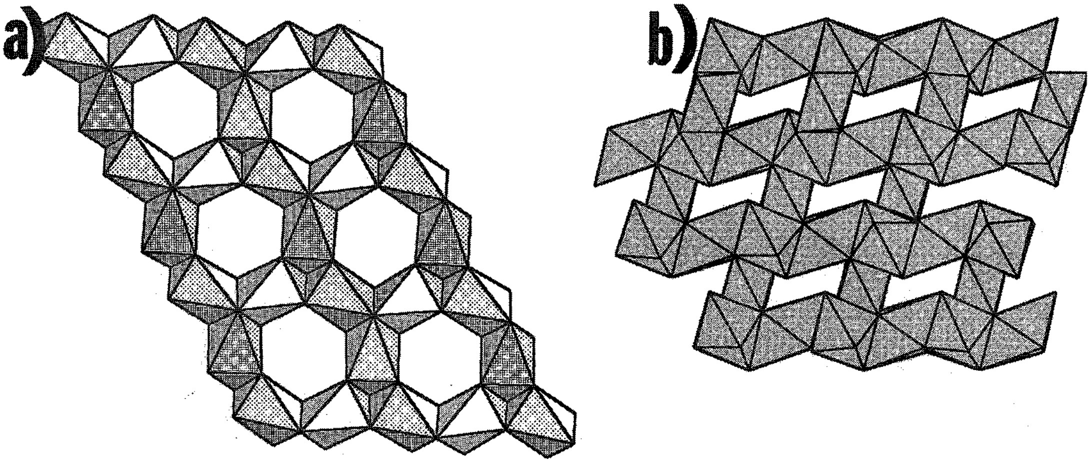

FIG. 4. The structure of paratacamite: (a) (001) projection showing the layer of edge-sharing $Cu(OH)_4Cl_2$ octahedra; (b) (110) projection showing (001) layering of $Cu(OH)_4Cl_2$ octahedra and isolated $Cu(OH)_6$ octahedra cross-linking layers. The *c* axis is vertical.

sidered as new minerals: 1) compositions between $Cu_3(Zn,Cu)(OH)_6Cl_2$ and $(Cu,Zn)_3Zn(OH)_6Cl_2$, which is the Zn analogue of paratacamite; these compositions correspond to those of minerals from the Kali Kafi mine, Anarak, Iran, and Herminia, Chile, with the latter described by Kracher & Pertlik (1983); 2) $(Cu,Ni)_3Ni(OH)_6Cl_2$, which is the mineral of this composition from the Carr Boyd nickel mine (Jambor *et al.* 1996), and from Widgiemooltha, Australia (Nickel *et al.* 1994).

ACKNOWLEDGEMENTS

The financial support of a Research Advisory Committee Grant from the Canadian Museum of Nature to JDG is gratefully acknowledged. The authors appreciate the careful reviews and helpful improvements of the two referees, Drs. Peter Burns and Frank Hawthorne, and the Editor, Dr. Robert Martin.

REFERENCES

BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.

EBY, R.K. & HAWTHORNE, F.C. (1993): Structural relations in copper oxysalt minerals. I. Structural hierarchy. *Acta Crystallogr.* **B49**, 28-56.

FLEET, M.E. (1975): The crystal structure of paratacamite, $Cu_2(OH)_3Cl$. *Acta Crystallogr.* **B31**, 183-187.

GABE, E.J., LE PAGE, Y., CHARLAND, J.-P., LEE, F.L. & WHITE, P.S. (1989): NRCVAX – an interactive system for structure analysis. *J. Appl. Crystallogr.* **33**, 384-387.

HAWTHORNE, F.C. (1985): Refinement of the crystal structure of botallackite. *Mineral. Mag.* **49**, 87-89.

———— & GRICE, J.D. (1990): Crystal-structure analysis as a chemical analytical method: application to light elements. *Can. Mineral.* **28**, 693-702.

JAMBOR, J.L., DUTRIZAC, J.E., ROBERTS, A.C., GRICE, J.D. & SZYMAŃSKI, J.T. (1996): Clinoatacamite, a new polymorph of $Cu_2(OH)_3Cl$, and its relationship to paratacamite and "anarakite". *Can. Mineral.* **34**, 61-72.

KRACHER, A. & PERTLIK, F. (1983): Zinkreicher Paratacamit, $Cu_3Zn(OH)_6Cl_2$, aus der Hermina Mine, Sierra Gorda, Chile. *Ann. Naturhist. Mus. Wien* **85/A**, 93-97.

LE PAGE, Y. (1987): Computer derivation of the symmetry elements implied in a structure description. *J. Appl. Crystallogr.* **20**, 264-269.

NICKEL, E.H., CLOUT, J.F.M. & GARTRELL, B.J. (1994): Secondary nickel minerals from Widgiemooltha, Western Australia. *Mineral. Rec.* **25**, 283-291, 302.

NORTH, A.C.T.. PHILLIPS, D.C. & MATHEWS, F.S. (1968): A semi-empirical method of absorption correction. *Acta Crystallogr.* **A24**, 351-359.

PARISE, J.B. & HYDE, B.G. (1986): The structure of atacamite and its relationship to spinel. *Acta Crystallogr.* **C42**, 1277-1280.

SHELDRICK, G.M. (1990): *SHELXTL, a Crystallographic Computing Package* (revision 4.1). Siemens Analytical Instruments, Inc., Madison, Wisconsin.

Received August 1, 1995, revised manuscript accepted September 27, 1995.