Mineralogy and Petrology (1987) 37: 89–96

Mineralogy and Petrology

Refinement of the Crystal Structure of Papagoite, $CaCuAlSi_2O_6(OH)_3$

L. A. Groat and F. C. Hawthorne

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada

With 4 Figures

Received January 15, 1987;
accepted May 5, 1987

Summary

The crystal structure of papagoite, $CaCuAlSi_2O_6(OH)_3$, monoclinic, a = 12.926 (3), b = 11.496 (3), c = 4.696 (1) Å, β = 100.81 (2)°, V = 685.4 (3) Å^3, space group $C2/m$, Z = 4, has been refined to an R index of 3.4% for 913 observed reflections measured with MoKα X-radiation. The single unique Cu cation is surrounded by six anions in a pseudo-octahedral arrangement showing strong Jahn-Teller distortion. Edge-sharing "rutile-like" chains of pseudo-octahedrally coordinated Cu and Al extend in the Y direction, and are cross-linked into an octahedral sheet by $Ca_2\varnothing_{10}$ ($\varnothing$ = unspecified ligand, O or OH) dimers. These sheets are linked by (Si_4O_{12}) rings to form a mixed tetrahedral-octahedral framework.

Zusammenfassung

Verfeinerung der Kristallstruktur von Papagoit, $CaCuAlSi_2O_6(OH)_3$

Die Kristallstruktur von Papagoit, $CaCuAlSi_2O_6(OH)_3$, monoklin a = 12,926 (3), b = 11.496 (3), c = 4.696 (1) Å, β = 100.81 (2)°, V = 685.4 (3) Å^3, Raumgruppe $C2/m$, Z = 4, wurde für 913 beobachtete, MoKα-Röntgenstrahlung gemessene Reflexe auf R = 3,4% verfeinert. Das eine symmetrieunabhängige Kupfer-Kation ist pseudooktaedrisch von sechs Anionen mit einer starken Jahn-Teller-Verzerrung umgeben. Die pseudo-oktaedrisch koordinierten Cu- und Al-Atome werden über Kanten zu parallel zur y-Achse verlaufenden „rutil-ähnlichen" Ketten verbunden, die zusammen mit den $Ca_2\varnothing_{10}$-Gruppen ($\varnothing$ = nicht spezifisierter Ligand, O bzw. OH) Oktaederschichten bilden. Diese Schichten werden durch (Si_4O_{12})-Ringe zu einem aus Tetraedern und Oktaedern bestehenden Netzwerk verknüpft.

Introduction

Papagoite is a rare calcium copper aluminium silicate first described by *Hutton* and *Vlisidis* (1960) from Ajo, Pima County, Arizona. It occurs as small (< 1 mm) blue equidimensional crystals associated with ajoite in veinlets and as veneers on slip-surfaces in altered quartz-albite rock. The structure was solved by *Guillebert* and *Le Bihan* (1965) using film techniques. As part of a general study of copper minerals (*Hawthorne,* 1985 a, b, 1986; *Hawthorne* and *Eby,* 1985; *Hawthorne* and *Groat,* 1985, 1986), the structure of papagoite is refined here.

Experimental Methods

The material used here is from Ajo, Pima County, Arizona; it has since been deposited at the Department of Mineralogy and Geology, Royal Ontario Museum, Toronto, catalogue number M 42656. The crystal selected for the data collection was mounted on a Nicolet *R* 3 *m* automated four-circle diffractometer and a random orientation rotation photograph was taken with graphite-monochromated molybdenum *Kα* X-rays. Twenty-five reflections were automatically centred, and least-squares refinement of the setting angles resulted in the (monoclinically constrained) cell dimensions given in Table 1, together with an orientation matrix relating the crystal axes and the diffractometer axes.

Table 1. *Miscellaneous Information for Papagoite*

a	12.926(3)Å	Crystal size	0.06x0.11x0.17mm
b	11.496(3)	Rad/Mono	Mo/Gr
c	4.696(1)	Total |Fo|	1061
β	100.81(2)°	|Fo|>3σ	913
V	685.4(3)Å^3	Final R (obs)	3.4%
Space group	C2/m	Final R_w (obs)	3.8%

Unit cell contents: $2[Ca_2Cu_2Al_2(Si_4O_{12})(OH)_6]$

$R = \Sigma(|Fo|-|Fc|)/\Sigma|Fo|$

$R_w = [\Sigma w(|Fo|-|Fc|)^2/\Sigma wFo^2]^{\frac{1}{2}}, w=1$

Temperature factor form used: $\exp(-2\pi^2[h^2a^{*2}U_{11}+....+2hka^*b^*U_{12}+....])$

Intensity data were collected according to the method of *Hawthorne* (1985 a). A total of 1 102 reflections were measured out to a maximum 2 θ of 60°. Ten strong reflections uniformily distributed with regard to 2 θ were measured at 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0–350°. These were used to model the crystal shape as an ellipsoid, with minimum and maximum transmissions of 0.765 and 0.557 respectively, reducing *R* (azimuthal) from 5.0 to 2.1%; this crystal shape was then used to apply an absorption correction to all of the intensities. The data were then corrected for Lorentz and polarization effects, and reduced to structure factors; of the 1 102 unique reflections, 913 were classed as observed (I > 2.5 σI).

Table 2. *Atomic Parameters for Papagoite*

	x	y	z	U_{eq}*
Ca	0	0.1553(1)	1/2	1.10(3)
Cu	0.26873(5)	1/2	0.4461(1)	0.77(2)
Al	1/4	1/4	1/2	0.51(4)
Si	0.38740(8)	0.13238(9)	0.0678(2)	0.49(2)
O(1)	0.2005(2)	0.3697(2)	0.2259(6)	0.86(7)
O(2)	0.1631(2)	0.1268(2)	0.3073(5)	0.74(7)
O(3)	0.4234(3)	1/2	0.2317(8)	0.80(10)
O(4)	0	0.3198(4)	0	1.10(10)
O(5)	0.3615(2)	0.2209(3)	0.3058(6)	0.89(7)
O(6)	0.4013(3)	0	0.1931(9)	1.10(10)

---

*$U_{eq} = (U_{11}U_{22}U_{33})^{1/3} \times 10^2$

Table 3. *Anisotropic Temperature Factor Coefficients for Papagoite*

	U_{11}^*	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	49(4)	97(5)	177(5)	0	6(4)	0
Cu	88(3)	49(3)	81(3)	0	-18(2)	0
Al	47(6)	59(7)	53(6)	7(5)	22(5)	-3(5)
Si	40(4)	54(4)	56(4)	-3(3)	11(3)	-9(3)
O(1)	101(12)	66(11)	79(11)	-2(10)	-18(9)	0(9)
O(2)	87(11)	65(11)	69(11)	-1(9)	2(9)	7(9)
O(3)	68(16)	72(16)	77(17)	0	-15(13)	0
O(4)	73(16)	106(18)	162(18)	0	45(14)	0
O(5)	76(12)	106(12)	95(12)	-1(10)	43(9)	-33(10)
O(6)	135(18)	74(17)	109(18)	0	-30(14)	0

---

*$U_{ij} = U_{ij} \times 10^4$

Refinement

Scattering curves for neutral atoms together with anomalous dispersion coefficients were taken from *Cromer* and *Mann* (1968) and *Cromer* and *Liberman* (1970). *R*-indices are of the form given in Table 1, and are expressed as percentages. Using the structure of *Guillebert* and *Le Bihan* (1965) as a starting model, refinement converged to an *R*-index of 3.4% with anisotropic temperature factors. Difference-Fourier maps showed weak maxima at the expected hydrogen atom positions; however, these would not remain stable on least-squares refinement, and hence the hydrogen atoms were not explicitely located. Final parameters are given in Tables 2 and 3; observed and calculated structure factors are available from the authors. Selected interatomic distances and angles are given in Table 4 and a bond valence analysis is given in Table 5.

Table 4. *Selected Interactomic Distances (Å) and Angles (°) in Papagoite*

Si-O(1)g	1.615(3)	Cu-O(1),b	1.936(3) x2
Si-O(4)g	1.642(2)	Cu-O(2)a,d	1.964(3) x2
Si-O(5)	1.592(3)	Cu-O(3)	2.402(4)
Si-O(6)	1.629(2)	Cu-O(6)a	3.016(5)
< Si-O >	1.620	< Cu-O >	2.203
Al-O(1),a	1.910(3) x2	Ca-O(2),c	2.467(3) x2
Al-O(2),a	1.925(3) x2	Ca-O(3)a,e	2.299(2) x2
Al-O(5),a	1.875(3) x2	Ca-O(5)a,f	2.334(3) x2
< Al-O >	1.904	< Ca-O >	2.367
O(1)g-O(4)g	2.672(3)	O(1)g-Si-O(4)g	110.3(1)
O(1)g-O(5)	2.685(4)	O(1)g-Si-O(5)	113.7(1)
O(1)g-O(6)	2.622(4)	O(1)g-Si-O(6)	107.8(2)
O(4)g-O(5)	2.539(3)	O(4)g-Si-O(5)	103.5(2)
O(4)g-O(6)	2.679(4)	O(4)g-Si-O(6)	110.0(2)
O(5)-O(6)	2.663(3)	O(5)-Si-O(6)	111.5(2)
< O-O >Si	2.643	< O-Si-O >	109.5
O(1)-O(2)	2.872(4) x2	O(1)-Al-O(2)	97.0(1) x2
O(1)-O(2)a	2.543(3) x2	O(1)-Al-O(2)a	83.0(1) x2
O(1)-O(5)	2.666(4) x2	O(1)-Al-O(5)	89.5(1) x2
O(1)-O(5)a	2.688(4) x2	O(1)-Al-O(5)a	90.5(1) x2
O(2)-O(5)	2.785(4) x2	O(2)-Al-O(5)	94.2(1) x2
O(2)-O(5)a	2.586(4) x2	O(2)-Al-O(5)a	85.8(1) x2
< O-O >Al	2.680	< O-Al-O >	90.0
O(1)-O(1)b	2.996(5)	O(1)-Cu-O(1)b	101.4(2)
O(1)-O(2)a	2.543(3) x2	O(1)-Cu-O(2)a	81.4(1) x2
O(1)-O(3)	3.243(4) x2	O(1)-Cu-O(3)	96.2(1) x2
O(1)-O(6)a	3.573(5) x2	O(1)-Cu-O(6)a	89.6(1) x2
O(2)a-O(2)d	2.915(5)	O(2)a-Cu-O(2)d	95.8(1)
O(2)a-O(3)	2.995(5) x2	O(2)a-Cu-O(3)	86.0(1) x2
O(2)a-O(6)a	3.539(6) x2	O(2)a-Cu-O(6)a	87.8(1) x2
< O-O > Cu	3.141	< O-Cu-O >	89.9
O(2)-O(3)a	2.995(5) x2	O(2)-Ca-O(3)a	77.8(1) x2
O(2)-O(3)e	3.380(4) x2	O(2)-Ca-O(3)e	90.3(1) x2
O(2)-O(5)a	2.586(4) x2	O(2)-Ca-O(5)a	65.1(1) x2
O(2)-O(5)f	4.273(6) x2	O(2)-Ca-O(5)f	125.7(1)
O(3)a-O(3)e	2.898(4)	O(3)a-Ca-O(3)e	77.8(1)
O(3)e-O(5)f	3.340(5) x2	O(3)e-Ca-O(5)f	92.4(1) x2
O(5)a-O(5)f	3.701(5)	O(5)a-Ca-O(5)f	104.9(1)
< O-O > Ca	3.309	< O-Ca-O >	90.4

Hydrogen bond contact: O(2)....O(3) 2.953(4)

a: $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; b: $x, 1-y, z$; c: $\bar{x}, y, 1-z$; d: $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$;
e: $-\frac{1}{2}+x, \frac{1}{2}+y, z$; f: $-\frac{1}{2}+x, \frac{1}{2}-y, z$; g: $\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$.

Description of the Structure

An ORTEP view (*Johnson*, 1976) of papagoite is shown in Fig. 1. There is one unique Si position in the structure; the ⟨Si—O⟩ distance of 1.620 Å is in line with the mean anion coordination number of 2.75, and the variation in bond lengths and angles (Table 4) fall well within the range typical of (SiO_4) tetrahedra (*Baur*, 1978). There is one unique Al position, and the Al is coordinated by four oxygens and two hydroxyls in a distorted octahedral arrangement with *trans* hydroxyl anions. The one unique Cu atom is surrounded by six anions from 1.936 (2) to

Table 5. *Bond Valence* Table for Papagoite*

	Cu	Ca	Si	Al	H(2)	H(3)	Σ
O(1)	$0.488^{x2}_{\downarrow}$		1.019	$0.496^{x2}_{\downarrow}$			2.003
O(2)	$0.448^{x2}_{\downarrow}$	$0.250^{x2}_{\downarrow}$		$0.480^{x2}_{\downarrow}$	0.782		2.0
O(3)	0.134	$0.366^{x2\rightarrow}_{\downarrow}$			0.218	1.0	2.084
O(4)			$0.949^{x2\rightarrow}$				1.898
O(5)		$0.338^{x2}_{\downarrow}$	1.083	$0.537^{x2}_{\downarrow}$			1.958
O(6)	0.034		$0.982^{x2\rightarrow}$				1.998
Σ	2.040	1.908	4.033	3.026	1.0	1.0	

*parameters from Brown (1981)

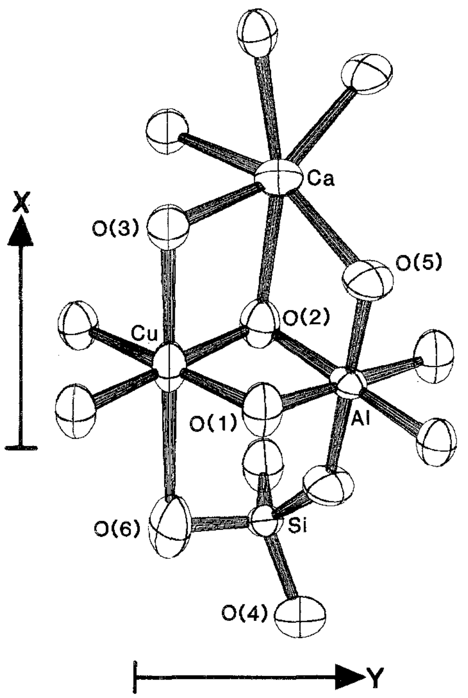

Fig. 1. Bond connectivity plot for papagoite, projected down Z

3.016 (5) Å; there are four meridional anions at about 1.95 Å with the axial anions much further away, a situation typical for Jahn-Teller distortion of an octahedral configuration. There is one unique Ca position surrounded by two oxygens and four hydroxyls in a considerably distorted octahedral arrangement; the two oxygens are in the *cis* configuration.

The bond valence distribution (Table 5) shows O (2) and O (3) to be hydroxyl ions. O (3) is bonded to the two Ca atoms, receiving a total bond valence contribution of 0.73 v. u. (valence units) from them, and one Cu, receiving a bond valence slip-surfaces in altered quartz-albite rock. The structure was solved by *Guillebert* and *Le Bihan* (1965) using film techniques. As part of a general study of copper minerals (*Hawthorne,* 1985 a, b, 1986; *Hawthorne* and *Eby,* 1985; *Hawthorne* and *Groat,* 1985, 1986), the structure of papagoite is refined here.

Experimental Methods

The material used here is from Ajo, Pima County, Arizona; it has since been deposited at the Department of Mineralogy and Geology, Royal Ontario Museum, Toronto, catalogue number M 42656. The crystal selected for the data collection was mounted on a Nicolet *R* 3 *m* automated four-circle diffractometer and a random orientation rotation photograph was taken with graphite-monochromated molybdenum *Kα* X-rays. Twenty-five reflections were automatically centred, and least-squares refinement of the setting angles resulted in the (monoclinically constrained) cell dimensions given in Table 1, together with an orientation matrix relating the crystal axes and the diffractometer axes.

Table 1. *Miscellaneous Information for Papagoite*

a	12.926(3)Å	Crystal size	0.06x0.11x0.17mm
b	11.496(3)	Rad/Mono	Mo/Gr
c	4.696(1)	Total |Fo|	1061
β	100.81(2)°	|Fo|>3σ	913
V	685.4(3)Å^3	Final R (obs)	3.4%
Space group	C2/m	Final R_w (obs)	3.8%

Unit cell contents: $2[Ca_2Cu_2Al_2(Si_4O_{12})(OH)_6]$

$R = \Sigma(|Fo|-|Fc|)/\Sigma|Fo|$

$R_w = [\Sigma w(|Fo|-|Fc|)^2/\Sigma wFo^2]^{\frac{1}{2}}, w=1$

Temperature factor form used: $\exp(-2\pi^2[h^2a^{*2}U_{11}+....+2hka^*b^*U_{12}+....])$

Intensity data were collected according to the method of *Hawthorne* (1985 a). A total of 1 102 reflections were measured out to a maximum 2 θ of 60°. Ten strong reflections uniformily distributed with regard to 2 θ were measured at 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0–350°. These were used to model the crystal shape as an ellipsoid, with minimum and maximum transmissions of 0.765 and 0.557 respectively, reducing *R* (azimuthal) from 5.0 to 2.1%; this crystal shape was then used to apply an absorption correction to all of the intensities. The data were then corrected for Lorentz and polarization effects, and reduced to structure factors; of the 1 102 unique reflections, 913 were classed as observed ($I > 2.5\,\sigma I$).

long meridional-apical edges of the $Cu\varnothing_6$ octahedron are shared with the much larger $Ca\varnothing_6$ octahedra such that the long Cu—$\varnothing$ (apical) distances from adjacent chains adjoin the short shared edge of the $Ca_2\varnothing_{10}$ dimer; thus the strongly elongated octahedra fit easily into the octahedral sheet.

Octahedral sheets are joined into a three-dimensional framework by four-membered (Si_4O_{12}) rings (Fig. 3) that share corners with adjacent sheets. The four-membered rings overlie the empty octahedral sites in the sheet and individual tetrahedra bridge along adjacent octahedra of the Cu—Al—Cu—Al edge-sharing chains. Both the along-chain linkage and the inter-sheet linkage can be seen in Fig. 4.

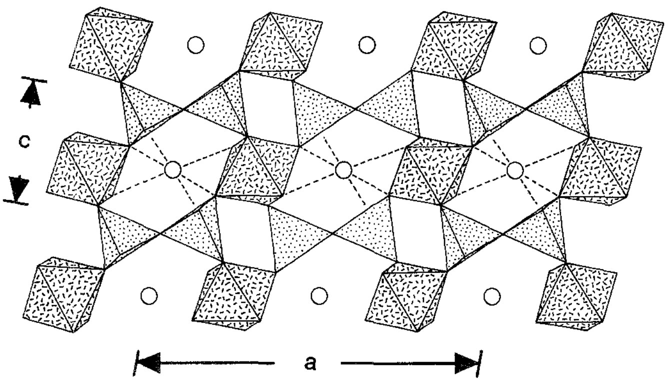

Fig. 4. Polyhedral representation of the papagoite structure projected down Y; legend as in Fig. 3

Papagoite can be considered to be a modified close-packed structure. This is seen in Fig. 2, in which the layered aspect of the structure is emphasized. The silicon atoms do not assume a normal close-packed position, as the O (4) anion that bridges part of the four-membered ring is inserted between the upper and lower anions of adjacent octahedral sheets.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada in the form of a graduate fellowship to L.A.G. and a fellowship, operating grant and major equipment grant to F.C.H.

References

Baur WH (1978) Variation of mean Si—O bond lengths in silicon-oxygen tetrahedra. Acta Cryst B 34: 1751–1756

Brown ID (1981) The bond-valence method: an empirical approach to chemical structure and bonding. In: Structure and bonding in crystals, II. Academic Press, New York

Cromer DT, Libermann D (1970) Relativistic calculation of anomalous scattering factors for X-rays. J Chem Phys 53: 1891–1898

— *Mann JB* (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. Acta Cryst A 24: 321–324

Guillebert C, Le Bihan M-T (1965) Contribution á l'étude structurale des silicates de cuivre: structure atomique de la papagoite. Bull Soc Franç Minér Crist LXXXVIII: 119–121

Hawthorne FC (1985 a) The crystal structure of stringhamite. Tschermaks Min Petr Mitt 34: 15–24

— (1985 b) The crystal structure of botallackite. Min Mag 49: 85–91

— (1986) Lammerite, $Cu_3(AsO_4)_2$ a modulated close-packed structure. Amer Min 71: 206–209

— *Eby R* (1985) Refinement of the structure of lindgrenite. N Jb Min Mh 1985: 234–240

— *Groat LA* (1985) The crystal structure of wroewolfeite, a mineral with $[(Cu_4(SO_4)(OH)_6(H_2O)]$ sheets. Amer Min 70: 1050–1055

— — (1986) The crystal structure and chemical composition of cumengéite. Min Mag 50: 157–162

Hutton CO, Vlisidis AC (1960) Papagoite, a new copper-bearing mineral from Ajo, Arizona. Amer Min 45: 599–611

Johnson CK (1976) ORTEP II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Authors' address: Dr. *L. A. Groat* and Dr. *F. C. Hawthorne,* Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada, R3T 2N2.