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JOHILLERITE FROM TOLBACHIK, KAMCHATKA PENINSULA, RUSSIA: CRYSTAL-STRUCTURE REFINEMENT AND CHEMICAL COMPOSITION

KIMBERLY T. TAIT¶ AND FRANK C. HAWTHORNE§

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

ABSTRACT

Johillerite from a fumarole in the North Breach of the Great Fissure Tolbachik eruption (GFTE), Kamchatka Peninsula, Russia, monoclinic, *a* 6.7520(14), *b* 12.739(3), *c* 11.068(2) Å, β 100.37(3)°, *V* 936.4(2) Å^3, *I*2/*a*, *Z* = 4 has been refined to an R_1 value of 3.2% for 1175 observed ($|F_o| \geq 4\sigma F$) reflections measured with a Bruker *P*4 diffractometer equipped with a CCD detector. The crystal used for the collection of the X-ray intensity data was subsequently analyzed with an electron microprobe; the resulting structural formula is $Na_{0.77}$ $K_{0.03}$ $Pb_{0.01}$ $Ca_{0.01}$ $Mn^{2+}_{0.01}$ $Zn_{0.13}$ $Mg_{2.18}$ $Cu^{2+}_{1.55}$ $Fe^{3+}_{0.26}$ $Al_{0.06}$ $(As^{5+}_{2.96}$ $P_{0.04})$ O_{12}. The unusual feature of the johillerite structure is the *A*(1)' site, a square-planar-coordinated site fully occupied by Cu^{2+}, that is displaced ¼ along *x*. The *A*(2) site is similar to that in other alluaudite-group minerals, surrounded by eight O-atoms with a <*A*(2)–O> distance of 2.70 Å, and occupied by Na plus small amounts of other large cations. The refined site-scattering values and observed <*M*–O> distances at the *M*(1) and *M*(2) sites are in accord with occupancy primarily by Mg, with Cu^{2+} at *M*(1) and Cu^{2+} + Fe^{3+} + Al at *M*(2). Relative to the compositions of the arsenate minerals arseniopleite and caryinite, Cu^{2+} has replaced Ca in the formula of johillerite. In arseniopleite and caryinite, Ca (+ Na) at the *A*(1) site is [7]- or [8]-coordinated, and the resulting sites occur in chains of edge-sharing coordination polyhedra extending in the *a* direction. Rather than replacing Ca at the center of the *A*(1) polyhedron, Cu^{2+} in johillerite occurs close to the edge shared between adjacent polyhedra, adopting square-planar coordination that is common for Cu^{2+}.

Keywords: johillerite, crystal structure, alluaudite group, Cu mineral, Kamchatka, Russia.

SOMMAIRE

Nous avons affiné la structure de la johillerite provenant d'une fumerole de la section égueulée nord de l'éruption fissurale de Tolbachik, péninsule de Kamchatka, en Russie, monoclinique, *a* 6.7520(14), *b* 12.739(3), *c* 11.068(2) Å, β 100.37(3)°, *V* 936.4(2) Å^3, *I*2/*a*, *Z* = 4, jusqu'à une valeur R_1 de 3.2% pour 1175 réflexions observées ($|F_o| \geq 4\sigma F$) et mesurées avec un diffractomètre Bruker *P*4 muni d'un détecteur CCD. Le cristal utilisé dans la collection des intensités en diffraction X a ensuite été analysé avec une microsonde électronique. La formule structurale qui en résulte est $Na_{0.77}$ $K_{0.03}$ $Pb_{0.01}$ $Ca_{0.01}$ $Mn^{2+}_{0.01}$ $Zn_{0.13}$ $Mg_{2.18}$ $Cu^{2+}_{1.55}$ $Fe^{3+}_{0.26}$ $Al_{0.06}$ $(As^{5+}_{2.96}$ $P_{0.04})$ O_{12}. L'aspect inhabituel de la structure de la johillerite porte sur le site *A*(1)', à coordinence en plan carré, déplacé par ¼ le long de *x*, qu'occupe complètement le Cu^{2+}. Le site *A*(2) ressemble à celui des autres membres du groupe de l'alluaudite; il est entouré de huit atomes d'oxygène avec une distance <*A*(2)–O> de 2.70 Å, et rempli par le Na et des quantités moindres d'autres cations à gros rayon. L'occupation affinée des sites *M*(1) et *M*(2), ainsi que les distances <*M*–O>, concordent avec la présence surtout de Mg, avec Cu^{2+} à *M*(1) et Cu^{2+} + Fe^{3+} + Al à *M*(2). Par rapport aux compositions des arsenates arsénioplèite et caryinite, le Cu^{2+} dans la formule de la johillerite a remplacé le Ca. Dans l'arsénioplèite et la caryinite, Ca (+ Na) au site *A*(1) possède une coordinence [7] ou [8], et les sites qui en résultent définissent des chaînes de polyèdres allongés le long de *a*. Plutôt que de remplacer le Ca au centre du polyèdre *A*(1), le Cu^{2+} dans la johillerite est situé près de l'arête partagée entre les polyèdres adjacents, où il adopte une coordinence en plan carré, comme c'est le cas courant dans les composés de Cu^{2+}.

(Traduit par la Rédaction)

Mots-clés: johillerite, structure cristalline, groupe de l'alluaudite, minéral de cuivre, Kamchatka, Russie.

¶ *Present address*: Department of Geosciences, University of Arizona, Tucson, Arizona 85721-0077, U.S.A.

§ *E-mail address*: frank_hawthorne@umanitoba.ca

INTRODUCTION

Johillerite, Na $(Mg,Zn)_3$ Cu^{2+} $(AsO_4)_3$ (Keller *et al.* 1982) , is an arsenate member of the alluaudite-group minerals originally described in an oxidized copper ore from Tsumeb, Namibia. Johillerite is closely related to o'danielite, Na Zn_3 H_2 $(AsO_4)_3$ (Keller *et al.* 1981, Keller & Hess 1988), and other arsenates and phosphates of the alluaudite-group (Antenucci *et al.* 1993, 1995, Auernhammer *et al.* 1993, Hatert *et al.* 2000, Khorari *et al.* 1997a, b, c, Leroux *et al.* 1995a, b, Warner *et al.* 1993, Yakubovich *et al.* 1977). As part of a general study on the alluaudite-group minerals (*sensu lato*), we have examined the crystal structure of johillerite from this new locality in order to derive detailed site-populations and further examine the incorporation of Cu^{2+} into the alluaudite-type structure.

OCCURRENCE

The Great Fissure Tolbachik eruption (GFTE) in the Kamchatka Peninsula, Russia, is the largest basaltic eruption in more than 200 years (Fedotov 1984). It was active in 1975–1976 and consisted of two breaches (North and South) and seven cones. Beginning in the late 1970s, fumarolic activity of the GFTE resulted in a unique assemblage of minerals, with two dozen new species discovered to date. Johillerite is associated with hematite, tenorite, lammerite, urusovite, orthoclase and bradaczekite, Na Cu_4 $(AsO_4)_3$ (Filatov *et al.* 2001), which is also an arsenate member of the alluaudite group.

EXPERIMENTAL

A crystal measuring 60 × 80 × 80 μm was attached to a glass fiber and mounted on a Bruker *P*4 diffractometer equipped with a CCD detector and Mo*K*α radiation. Intensity data were collected and processed according to the procedure described by Cooper & Hawthorne (2001). Cell dimensions are reported in Table 1. The data were corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. A total of 4882 reflections was measured out to 60.10° 2θ using 60 s per frame, with index ranges $\bar{9} \le h \le 9$, $\overline{17} \le k \le 15$, $\overline{15} \le l \le 15$. Of the 1373 unique reflections, 1175 reflections were considered as observed ($|F_o| \ge 4\sigma F$).

TABLE 1. MISCELLANEOUS INFORMATION FOR JOHILLERITE

a (Å)	6.7520(14)	crystal size (μm)	60 x 80 x 80
b	12.739(3)	radiation	Mo*K*α/Gr
c	11.068(2)	No. of reflections	4772
V (Å³)	936.4(2)	No. unique reflections	1373
β	100.37(3)	Refinement method	Least squares on F^2; fixed weights ∝ 1/σ(*F*)
Space Group	*I*2/*a*	No. $\lvert F_o \rvert > 4\sigma F$	1175
Z	4	R_{merge} %	4.1
μ (mm⁻¹)	13.63	R_1 ($\lvert F_o \rvert > 4\sigma F$) %	3.2
D_{calc} (g/cm³)	4.38	wR_2 (F_o^2) %	7.6

$R = \Sigma(|F_o|-|F_c|) / \Sigma|F_o|$

$wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{½}$, $w = 1 / \sigma F_o^2$

The crystal used for X-ray diffraction was mounted on a Perspex disc, ground, polished, carbon-coated and analyzed with a Cameca SX–50 electron microprobe operating under the following conditions in wavelength-dispersion mode: acceleration voltage: 15 kV, beam current 20 nA, beam size: 15 μm, peak count-time: 20 s, background count-time: 10 s. The following standards and crystals were used for *K*α X-ray lines of the elements sought: Na: maričite, TAP; Mg: forsterite, TAP; Si: diopside, PET; P: maričite, PET; Ca: apatite, PET; Mn: spessartine, LiF; Fe: maričite, LiF; Zn: gahnite, LIF; As: mimetite, TAP. Ten points were analyzed, and the mean chemical composition is given in Table 2. The stereochemical details of johillerite indicate that Cu is in the divalent state. As the *f*(O_2) required for the reaction $Cu^+ \rightarrow Cu^{2+}$ is higher than that required for the reaction $Fe^{2+} \rightarrow Fe^{3+}$, it is likely that Fe is in the trivalent state, and the empirical formula was calculated accordingly. The resulting formula, calculated on the basis of As + P = 3.0 *apfu*, is $Na_{0.77}$ $K_{0.03}$ $Pb_{0.01}$ $Ca_{0.01}$ $Mn^{2+}{}_{0.01}$ $Zn_{0.13}$ $Mg_{2.18}$ $Cu^{2+}{}_{1.55}$ $Fe^{3+}{}_{0.26}$ $Al_{0.06}$ $(As^{5+}{}_{2.96}$ $P_{0.04})$ O_{12}.

CRYSTAL-STRUCTURE REFINEMENT

All calculations were done with the SHELXTL PC (Plus) system of programs; *R* indices are of the form given in Table 1 and are expressed as percentages. The crystal-structure refinement was initiated with the atom

TABLE 2. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA* (*apfu*) FOR JOHILLERITE FROM THE KAMCHATKA PENINSULA AND TSUMEB**

	Kamchatka	Tsumeb		Kamchatka	Tsumeb
As_2O_5	55.47	55.8	As	2.96	3.00
P_2O_5	0.47	–	P	0.04	–
PbO	0.23	–	Σ*T*	3.00	3.00
ZnO	1.75	5.4			
CuO	20.13	15.8	Pb	0.01	–
Fe_2O_3	3.41	–	Zn	0.13	0.41
MnO	0.10	–	Cu	1.55	1.23
CaO	0.10	–	Fe^{3+}	0.26	–
K_2O	0.25	–	Mn^{2+}	0.01	–
Al_2O_3	0.46	–	Ca	0.01	–
MgO	14.36	18.3	K	0.03	–
Na_2O	3.88	5.4	Al	0.06	–
TOTAL	100.61	100.7	Mg	2.18	2.81
			Na	0.77	1.08
			Σ	5.01	5.53

* Normalized on As + P = 3 *apfu*

** Taken from Keller *et al.* (1982)

TABLE 3. ATOM COORDINATES AND ANISOTROPIC-DISPLACEMENT PARAMETERS FOR JOHILLERITE

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
A(1)'	¼	0.00236(5)	½	0.0206(4)	0.0060(3)	0.0111(4)	0	0.0021(3)	0	0.0126(2)
A(2)	¼	0.0071(3)	0	0.038(2)	0.044(3)	0.0186(19)	0	0.0077(15)	0	0.0329(14)
M(1)	¼	0.73963(10)	0	0.0212(8)	0.0155(7)	0.0131(7)	0	–0.0001(5)	0	0.0170(5)
M(2)	0.08832(12)	0.15530(6)	0.21465(7)	0.0192(5)	0.0096(4)	0.0120(4)	0.0010(3)	0.0011(3)	–0.0004(3)	0.0138(3)
T(1)	¼	0.28556(4)	0	0.0157(3)	0.0073(2)	0.0106(3)	0	0.00495(19)	0	0.01089(15)
T(2)	0.10551(6)	0.88564(3)	0.23053(3)	0.0150(2)	0.0078(2)	0.0105(2)	–0.00067(12)	0.00335(14)	–0.00062(13)	0.01094(13)
O(1)	0.0537(5)	1.00302(19)	0.1679(3)	0.0232(15)	0.0075(12)	0.0209(15)	0.0011(10)	0.0048(12)	0.0026(10)	0.0171(6)
O(2)	0.3030(5)	–0.10913(18)	0.6161(3)	0.0233(15)	0.0097(13)	0.0093(12)	0.0009(9)	0.0008(11)	–0.0004(10)	0.0144(6)
O(3)	0.1564(4)	0.37986(19)	–0.1062(3)	0.0194(14)	0.0075(12)	0.0110(12)	0.0010(9)	0.0009(10)	0.0029(10)	0.0129(5)
O(4)	0.2783(4)	0.8299(2)	0.1588(2)	0.0174(14)	0.0118(12)	0.0152(13)	–0.0029(10)	0.0056(11)	0.0002(10)	0.0145(5)
O(5)	–0.1034(4)	0.8113(2)	0.2156(3)	0.0169(14)	0.0124(12)	0.0137(13)	–0.0018(10)	0.0046(10)	–0.0041(10)	0.0141(5)
O(6)	0.4394(4)	0.21446(19)	–0.0374(2)	0.0180(14)	0.0117(12)	0.0103(12)	–0.0009(9)	0.0046(10)	0.0019(10)	0.0131(5)

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN JOHILLERITE

A(1)'–O(2)a	x2	1.906(3)	*A*(2)–O(1)d,i	x2	2.470(3)
A(1)'–O(3)b,c	x2	1.941(3)	*A*(2)–O(1)f,j	x2	2.511(3)
<*A*(1)'–O>		1.924	*A*(2)–O(4)i,d	x2	2.846(4)
			A(2)–O(6)a	x2	2.996(4)
A(1)'–O(3)l,m	x2	3.537(3)	<*A*(2)–O>		2.706
M(2)–O(1)d		2.010(3)	*T*(2)–O(1)		1.659(3)
M(2)–O(3)c		2.003(3)	*T*(2)–O(2)k		1.700(3)
M(2)–O(4)e		2.082(3)	*T*(2)–O(4)		1.682(3)
M(2)–O(5)f		2.123(3)	*T*(2)–O(5)		1.682(3)
M(2)–O(5)g		2.128(3)	<*T*(2)–O>		1.681
M(2)–O(6)a		2.078(3)			
<*M*(2)–O>		2.071			
M(1)–O(2)a	x2	2.092(3)	*T*(1)–O(3)a	x2	1.720(3)
M(1)–O(4)c	x2	2.081(3)	*T*(1)–O(6)a	x2	1.678(3)
M(1)–O(6)e,h	x2	2.145(3)	<*T*(1)–O>		1.699
<*M*(1)–O>		2.106			

a: –*x*+½, *y*, –*z*+1; b: –*x*+½, –*y*+½, –*z*+½; c: *x*, –*y*+½, *z*+½; d: *x*, *y*–1, *z*; e: *x*–½, –*y*+1, *z*; f: *x*+½, –*y*+1, *z*; g: –*x*, *y*–½, *z*+½; h: –*x*+1, –*y*+1, –*z*; i: –*x*+½, –*y*+1, –*z*; j: –*x*, –*y*+1, –*z*; k: –*x*+½, *y*+1, –*z*+1; l: *x*+½, *y*–½, *z*+½; m: –*x*, *y*–½, –*z*+½

coordinates of caryinite (Ercit 1993), using the site nomenclature of Hatert *et al.* (2000). Note that the orientation chosen is conformable with the *I*2/*a* orientation adopted for caryinite (Ercit 1993) and arseniopleite (Tait & Hawthorne 2003), and the $P2_1/n$ orientation used by Ercit *et al.* (1986a, b) for bobfergusonite.

Full-matrix least-squares refinement of all positional, anisotropic-displacement and site-occupancy variables converged to an R_1 index of 3.2%. Refined coordinates and anisotropic-displacement factors are listed in Table 3, selected interatomic distances are given in Table 4, site-scattering values and assigned site-populations are given in Table 5, and a bond-valence table is shown as Table 6. Observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

DISCUSSION

The cation sites

The *T* sites are each surrounded by a tetrahedral arrangement of O atoms with <*T*–O> distances of 1.699 and 1.681 Å, respectively; the observed scattering values and <*T*–O> distances are in accord with occupancy of the *T* sites by As^{5+} (plus very minor P, Table 2). There are four additional occupied cation sites in johillerite, labeled *A*(1)', *A*(2), *M*(1) and *M*(2). The *A*(1)' site is surrounded by six anions in an octahedral arrangement, with four equatorial O atoms at 1.906 (×2) and 1.94 Å (×2) and two apical O atoms at 3.537(3) Å. The refined scattering at the *A*(1)' site is 29.1(1) *epfu* (electrons per formula unit), in exact accord with complete occupancy of this site by Cu. Moreover, the observed coordination of four short equatorial bonds and two long apical distances (Keller & Hess 1988) is typical for octahedrally coordinated Cu^{2+}, which always shows such Jahn–Teller distorted coordination (Jahn & Teller 1937, Burns & Hawthorne 1996). Inspection of the bond valences around both the *A*(1)' and O(3) sites (Table 6) shows that the long *A*(1)'–O(3) distance is too long to be considered as a bond: the calculated *A*(1)'–O(3) bond-valence is very low (0.013 valence units, *vu*) and the incident bond-valence sums at both *A*(1)' and O(3) are close to ideal without considering any possible contribution from a long *A*(1)'–O(3) bond. Hence the Cu^{2+} at the *A*(1)' site can be considered as square-planar [4]-coordinated.

The remaining cations to be assigned in the unit formula of johillerite are Cu^{2+}, Mg and Na, together with minor amounts of Fe, Zn, Mn, Ca, K and Pb (Table 2). As the mean bond-lengths at the *A*(2), *M*(1) and *M*(2) sites are 2.706, 2.106 and 2.071 Å, respectively, the small cations (Cu^{2+}, Mg, Fe^{3+}, Zn and Mn^{2+}) must occur at the *M*(1) and *M*(2) sites, and the large cations (Na plus minor Pb, K and Ca) must occur at the *A*(2) site. The multiplicity of the *M*(2) site is twice that of the *M*(1) site, and the refined site-scattering value at the *M*(2) site

TABLE 5. REFINED SITE–SCATTERING VALUES (RSS, *epfu*), MEAN BOND-LENGTHS (Å), ASSIGNED SITE-POPULATIONS (*apfu*) AND CORRESPONDING CALCULATED SITE-SCATTERING VALUES (CSS, *epfu*) FOR JOHILLERITE

Site	RSS	<*M*,*X*–O>	Site-populations	CSS	Group
A(1)′	29.1(1)	1.924	1.0 Cu^{2+}	29	*B*
A(2)	8.5(1)	2.706	0.77 Na + 0.01 Pb^{2+} + 0.01 Ca + 0.03 K	10.1	*A*
M(1)*	16.8(2)	2.106	0.79 Mg + 0.21 Cu^{2+}	15.6	*C*
M(2)*	36.6(3)	2.071	1.30 Mg + 0.39 Cu^{2+} + 0.25 Fe^{3+} + 0.06 Al	34.2	*D*

* the Cu^{2+} includes 0.12 Zn + 0.01 Mn *apfu*

TABLE 6. BOND-VALENCES (*vu*) FOR JOHILLERITE*

	A(1)′	*A*(2)	*M*(1)	*M*(2)	*T*(1)	*T*(2)	Σ
O(1)		$0.147^{\times2}\downarrow$ $0.136^{\times2}\downarrow$		0.410		1.356	2.049
O(2)	$0.536^{\times2}\downarrow$		$0.330^{\times2}\downarrow$			1.171	2.037
O(3)	$0.481^{\times2}\downarrow$			0.416	$1.091^{\times2}\downarrow$		1.998
O(4)		$0.076^{\times2}\downarrow$	$0.338^{\times2}\downarrow$	0.346		1.248	2.008
O(5)				0.315 0.311		1.248	1.874
O(6)		$0.060^{\times2}\downarrow$	$0.294^{\times2}\downarrow$	0.349	$1.265^{\times2}\downarrow$		1.968
	2.034 (2.000)**	0.838 (0.840)	1.924 (2.000)	2.147 (2.155)	4.712 (5.000)	5.023 (5.000)	

* calculated with the curves of Brown (1981);
** values in parantheses are the aggregate valence of the cations assigned to those sites (Table 5).

is significantly more than twice the refined site-scattering value at the *M*(1) site. Hence the more strongly scattering cations must be more strongly ordered at the *M*(2) site than at the *M*(1) site. The sum of the medium-sized divalent cations is 4.19 *apfu*; if the amounts of these cations are normalized to 4.00 *apfu* and Zn is combined with Cu^{2+}, Fe^{3+} can be assigned to the *M*(2) site on the argument that the <*M*(2)–O> distance is shorter than the <*M*(1)–O> distance (Table 4); the amounts of Cu^{2+} and Mg at these sites can then be calculated from the refined site-scattering values. The remaining large cations are assigned to the *A*(2) site on the basis of the large <*A*(2)–O> distance (Table 4). The resulting number of electrons per formula unit at the *A*(2) site (10.3 *epfu*) is somewhat higher than the refined value of 8.5 *epfu*; this anomaly may result from positional disorder at the *A*(2) site (see the large anisotropic-displacement values at this site, Table 3). The final assigned site-populations are given in Table 5.

Structure topology

The alluaudite structure has been well described elsewhere (Moore 1971, Ercit 1993, Khorari *et al.* 1997a, Tait & Hawthorne 2003), and will be examined only to illustrate the differences between the johillerite and alluaudite structures that result from the presence of Cu^{2+} in the former structure. In johillerite, Cu^{2+} replaces (Ca, Na) as an *A*-group cation. In most of the alluaudite-group minerals, the *A*-group cations occur at the *A*(1) site and are coordinated by seven or eight anions at a mean distance of ~2.5 Å (although several synthetic compounds have a coordination of [6] at *A*(1): Hatert *et al.* 2000). How does a small cation like Cu^{2+} replace large cations such as Ca and Na in such a large coordination polyhedron? The mechanism whereby this is done is illustrated in Figure 1. In alluaudite, the $A(1)O_{7-8}$ polyhedra share edges with each other to form a chain that extends in the *a* direction (Fig. 1a). The configuration surrounding Cu^{2+} in johillerite is shown in Figure 1b. Cu^{2+} does not actually replace (Ca, Na) at the center of the $A(1)O_{7-8}$ polyhedron; instead, Cu^{2+} occurs at the shared edges between adjacent polyhedra [the *A*(1)' site], adopting essentially a square-planar coordination with two very long apical anions that do not bond to Cu^{2+}.

Relation to other species

The end-member formula for johillerite is Cu^{2+} Na Mg_3 $(AsO_4)_3$. Filatov *et al.* (2001) recently reported the new mineral bradaczekite, Na Cu^{2+}_4 $(AsO_4)_3$, from the Tolbachik volcano, Kamchatka Peninsula, Russia, the same locality as the johillerite crystals examined here. On the basis of the structure of bradaczekite (Krivovichev *et al.* 2001) and its synthetic equivalent (Pertlik 1987), the formula of bradaczekite would be better written as Cu^{2+} Na Cu^{2+}_3 $(AsO_4)_3$. It is apparent that johillerite from this locality shows significant solid-solution toward bradaczekite (Table 2), as there is significant Cu^{2+} at the *M*(2) site, and substitution at the *M*(1) site is presumably also possible (as inferred from the existence of bradaczekite).

This replacement of (Ca, Na) by Cu^{2+} at the *A*(1)' site in this structure type is a rather novel substitution. Within a single chain, partial substitution of (Ca, Na) by Cu^{2+} does not seem possible, as it would lead to unacceptably close cation–cation approaches. On the other hand, omission of additional Ca and incorporation of H to satisfy local bond-valence requirements and maintain electroneutrality might allow a more complicated mechanism to occur. Also, partial replacement of (Ca, Na) by Cu^{2+} might occur through continuous chains of (Ca, Na) cations and also of Cu^{2+} cations. However, the current absence of compositions intermediate between caryinite or arseniopleite and johillerite argues for the lack of such complicated mechanisms discussed above and suggests that the close cation–cation approaches required by such a solid solution preclude its existence.

Warner *et al.* (1993) synthesized $Cu_{1.35}$ Fe_3 $(PO_4)_3$ and Cu_2 Mg_3 $(PO_4)_3$ with the alluaudite-type structure. In these structures, Cu^{2+} occurs in square-planar coordination, as is the case also in johillerite (Keller & Hess 1988, this study). However, these structures also contain Cu^+ [and Ag^+, Riffel *et al.* 1985)] in the linear [2]-coordination typical of this cation, indicating that the alluaudite structure-type can incorporate variable amounts of Cu by other mechanisms than the substitutions identified in johillerite. However, these compounds were synthesized in an argon atmosphere at low oxygen fugacity. These conditions are unlikely to be realized in the type of environments in which the alluaudite minerals normally crystallize, and incorporation of Cu^+ into minerals of this group seems unlikely. Nevertheless, the incorporation of Cu^{2+} into johillerite and nickenichite (Auernhammer *et al.* 1993) and of Cu^+ and Cu^{2+} into synthetic alluaudite-like compounds (Riffel *et al.* 1985, Pertlik 1987, Effenberger 1988, Warner *et al.* 1993) demonstrate the flexibility of the alluaudite structure-type in accommodating cations of unusual electronic structure and valence state.

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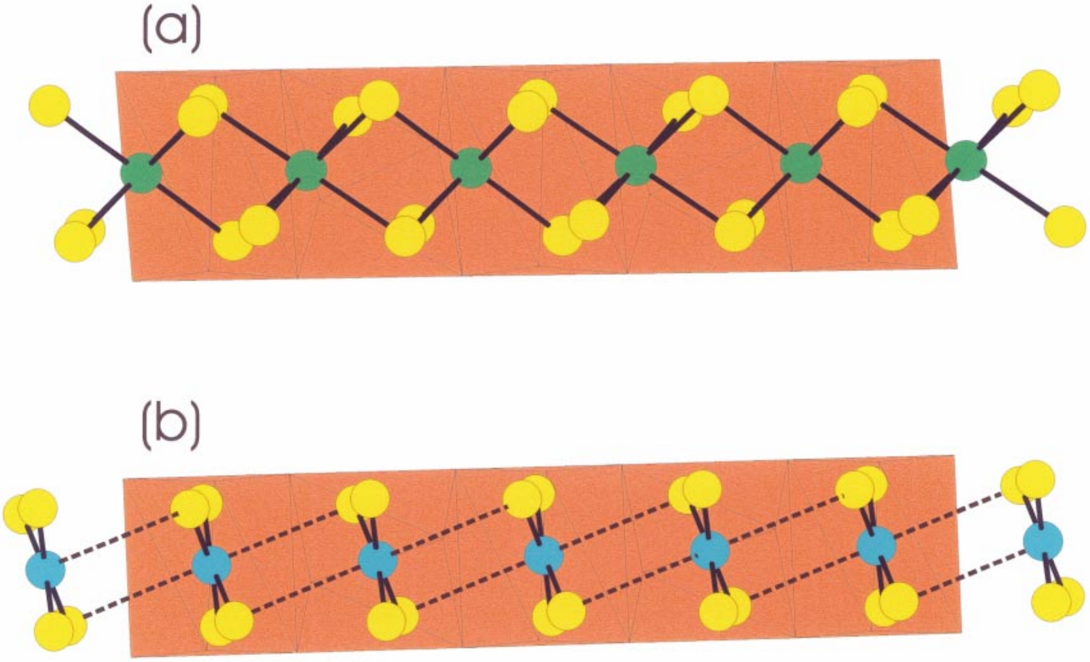

FIG. 1. (a) The chain of edge-sharing $A(1)O_{7-8}$ polyhedra in alluaudite, showing both the $A(2)O_8$ polyhedra (orange), the $A(1)'$ site (green circles: Ca,Na), its coordinating O atoms (yellow circles) and the $A(1)$–O bonds (black lines). (b) The chain of edge-sharing $A(1)'O_{4+2}$ polyhedra in johillerite, showing the $A(2)O_8$ polyhedra, the $A(1)'$ site (blue circles: Cu^{2+}), and the long $A(1)'$–O distances as broken lines.

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