

REFINEMENT OF THE CRYSTAL STRUCTURE OF ARSENIOPLEITE: CONFIRMATION OF ITS STATUS AS A VALID SPECIES

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ABSTRACT

Arseniopleite, ideally $(\text{Ca,Na})(\text{Na,Pb}^{2+})\text{Mn}^{2+}(\text{Mn}^{2+},\text{Mg,Fe}^{2+})_2\text{As}_3\text{O}_{12}$, is monoclinic, a 6.8113(6), b 13.0358(11), c 11.3245(10) Å, β 100.25(3)°, V 989.5(1) Å³, $I2/a$, $Z = 2$, has been refined to an R index of 2.3% for 1280 observed ($|F_o| \geq 4\sigma F$) reflections measured with a Bruker $P4$ diffractometer equipped with a CCD detector and $\text{MoK}\alpha$ X-radiation. The crystal used for the collection of the X-ray intensity data was subsequently analyzed with an electron microprobe. In arseniopleite, the $M(1)$ site is octahedrally coordinated and is occupied completely by Mn^{2+} with an observed $\langle M(1)\text{--O} \rangle$ distance of 2.218 Å. The $M(2)$ site is also octahedrally coordinated and is occupied by Mn^{2+} , Mg and Fe^{3+} with a $\langle M(2)\text{--O} \rangle$ distance of 2.129 Å. The $X(1)$ site is disordered off its ideal special position, locally decreasing its coordination number from [8] to [7]; $X(1)$ is occupied by dominant Ca and less Na, with a $\langle X(1)\text{--O} \rangle$ distance of 2.584 Å. The $X(2)$ site is [8]-coordinated with a $\langle X(2)\text{--O} \rangle$ distance of 2.732 Å, and is occupied predominantly by Na, with minor Pb^{2+} and Ba. The resulting unit formula is $(\text{Ca}_{0.68}\text{Na}_{0.32})(\text{Na}_{0.93}\text{Pb}^{2+}_{0.06}\text{Ba}_{0.01})\text{Mn}^{2+}(\text{Mn}^{2+}_{1.21}\text{Mg}_{0.52}\text{Fe}^{3+}_{0.27})(\text{As}_{2.98}\text{P}_{0.02})\text{O}_{12}$. Hence arseniopleite is confirmed as a valid mineral species distinct from caryinite. Arseniopleite has Mn^{2+} dominant at $M(1)$, and caryinite has Ca dominant at $M(1)$. The end-member compositions for these species are as follows: arseniopleite: $\text{Ca Na Mn}^{2+} \text{Mn}^{2+}_2 \text{As}_3 \text{O}_{12}$; caryinite: $\text{Ca Na Ca Mn}^{2+}_2 \text{As}_3 \text{O}_{12}$.

Keywords: arseniopleite, crystal structure, arsenate, alluaudite, caryinite, Örebro, Sweden.

SOMMAIRE

L'arséniopléite, dont la formule idéale est $(\text{Ca,Na})(\text{Na,Pb}^{2+})\text{Mn}^{2+}(\text{Mn}^{2+},\text{Mg,Fe}^{2+})_2\text{As}_3\text{O}_{12}$, est monoclinique, a 6.8113(6), b 13.0358(11), c 11.3245(10) Å, β 100.25(3)°, V 989.5(1) Å³, $I2/a$, $Z = 2$; nous l'avons affiné jusqu'à un résidu R de 2.3% pour 1280 réflexions observées ($|F_o| \geq 4\sigma F$) mesurées avec un diffractomètre Bruker $P4$ muni d'un détecteur de type CCD (rayonnement $\text{MoK}\alpha$). Le cristal utilisé pour le prélèvement des intensités des rayons X a par la suite été analysé avec une microsonde électronique. Dans l'arséniopléite, le site $M(1)$ possède une coordination octaédrique; il est occupé complètement par le Mn^{2+} , avec une distance $\langle M(1)\text{--O} \rangle$ de 2.218 Å. Le site $M(2)$ possède aussi une coordination octaédrique et contient Mn^{2+} , Mg et Fe^{3+} , la distance $\langle M(2)\text{--O} \rangle$ étant 2.129 Å. Le site $X(1)$ est déplacé de sa position spéciale idéale, ce qui localement diminue la coordination de [8] à [7]; $X(1)$ contient surtout le Ca et, à un degré moindre, Na, avec une distance $\langle X(1)\text{--O} \rangle$ de 2.584 Å. Le site $X(2)$ possède une coordination [8], et la distance $\langle X(2)\text{--O} \rangle$ est 2.732 Å. Le site contient surtout Na, avec des quantités mineures de Pb^{2+} et Ba. La formule empirique est $(\text{Ca}_{0.68}\text{Na}_{0.32})(\text{Na}_{0.93}\text{Pb}^{2+}_{0.06}\text{Ba}_{0.01})\text{Mn}^{2+}(\text{Mn}^{2+}_{1.21}\text{Mg}_{0.52}\text{Fe}^{3+}_{0.27})(\text{As}_{2.98}\text{P}_{0.02})\text{O}_{12}$. L'arséniopléite est donc confirmée comme espèce minérale valide, distincte de la caryinite. Dans l'arséniopléite, le Mn^{2+} prédomine au site $M(1)$, tandis que dans la caryinite, c'est le Ca qui est dominant. La composition idéale de ces espèces est comme suit: arséniopléite: $\text{Ca Na Mn}^{2+} \text{Mn}^{2+}_2 \text{As}_3 \text{O}_{12}$; caryinite: $\text{Ca Na Ca Mn}^{2+}_2 \text{As}_3 \text{O}_{12}$.

(Traduit par la Rédaction)

Mots-clés: arséniopléite, structure cristalline, arsenate, alluaudite, caryinite, Örebro, Suède.

INTRODUCTION

Arseniopleite is an arsenate member of the alluaudite-group minerals. It was originally described by Igelström (1888) from the Sjö mine, near Grythyttan, Örebro, Sweden. Moore (1968) showed that arseniopleite and caryinite are structurally related, and proposed that

arseniopleite is a "water-rich" variety of caryinite. Keller & Hess (1988) showed that the arsenates o'danielite and johillerite are isostructural with alluaudite (Moore 1971), and there has been much work on synthetic alluaudite-like arsenates (Keller *et al.* 1981, Winand *et al.* 1990, Khorari *et al.* 1995, 1997a, b, c, 1998, Stock *et al.* 2001). Dunn & Peacor (1987) re-

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examined caryinite (Lundström 1874, Sjögren 1895) from Långban, Sweden, and arseniopleite from Långban and from the Sjö mine, Sweden, and confirmed the observation of Moore (1968) that both caryinite and arseniopleite are isostructural, and showed that both are isostructural with alluaudite (Strunz 1960, Fisher 1962). They also showed that the analytical data of Igelström (1888) and the conclusion of Moore (1968) that arseniopleite contains "water" are not correct; the analytical work of Dunn & Peacor (1987) shows both caryinite and arseniopleite to be anhydrous. Dunn & Peacor (1987) re-analyzed both arseniopleite and caryinite; they stated that "If the cation assignments follow the scheme proposed by Moore (1968) for alluaudite, then (their formula for arseniopleite) might define arseniopleite as a species with Mn dominant in the $M(1)$ site instead of Ca/Mn which apparently occupies that site in caryinite". However, they stressed that until such a site-occupancy is confirmed, the species status of arseniopleite remains uncertain. Ericit (1993) refined the crystal structure of caryinite from Långban, Sweden; he showed that the $M(1)$ site is occupied by Ca and Mn^{2+} with Ca dominant, and supported the proposal of Dunn & Peacor (1987) that arseniopleite is isostructural with caryinite (and alluaudite) with Mn^{2+} dominant at $M(1)$. However, the status of arseniopleite is still considered somewhat uncertain (Nysten *et al.* 1999). As part of a general study of the alluaudite-group minerals (*sensu lato*), we have refined the crystal structure of arseniopleite in order to derive detailed site-populations and to resolve the issue of its species status.

EXPERIMENTAL

The specimen of arseniopleite used in this work is the original sample of Igelström (1888) and was obtained from Mr. William W. Pinch of Rochester, New York.

A crystal measuring $80 \times 80 \times 120 \mu\text{m}$ was attached to a glass fiber and mounted on a Bruker *P4*

diffractometer equipped with a CCD detector and $\text{MoK}\alpha$ X-radiation. Intensity data were collected and processed according to the procedure described by Cooper & Hawthorne (2001). The data were corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. A total of 5115 reflections was measured out to $60.10^\circ 2\theta$ using 60 s per frame, with index ranges $16 \leq h \leq 17$, $17 \leq k \leq 18$, $9 \leq l \leq 9$. Of the 1453 unique reflections, 1282 reflections were considered as observed [$|F_o| \geq 4\sigma F$]. Miscellaneous information related to data collection and crystal-structure refinement is listed in Table 1.

The crystal used for X-ray diffraction was mounted in 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: excitation voltage: 15 kV, specimen current 20 nA, beam size: $15 \mu\text{m}$, peak count-time: 20 s, background count-time: 10 s. The following standards and crystals were used for $K\alpha$ X-ray lines for 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; Ba: barite, LiF; Pb: mimetite, PET. Cl, F, Sr, K and Al were sought, but were not detected. Ten points were analyzed, and the mean chemical composition is given in Table 2. The unit formula was calculated on the basis of 12 anions: $(\text{Ca}_{0.68} \text{Na}_{0.25} \text{Mn}_{0.01}) (\text{Na}_{0.93} \text{Pb}_{0.06} \text{Ba}_{0.01}) \text{Mn} (\text{Mn}_{1.22} \text{Mg}_{0.53} \text{Fe}_{0.27})_2 (\text{As}_{3.01} \text{Si}_{0.02} \text{P}_{0.02}) \text{O}_{12}$.

CRYSTAL-STRUCTURE REFINEMENT

Cell orientation

A significant issue in the refinement of arseniopleite (and work on all the alluaudite-structure minerals *sensu lato*) is the choice of cell orientation. Boström (1957) determined the space group of caryinite as $P2_1/c$, but

TABLE 1. MISCELLANEOUS INFORMATION FOR ARSENIOPLEITE

a (Å)	6.8113(6)	crystal size (mm)	0.08 x 0.08 x 0.12
b	13.0358(11)	Radiation	$\text{MoK}\alpha/\text{graphite}$
c	11.3245(10)	2θ -range for data collection ($^\circ$)	60.1
β	100.25(3)	$R(\text{int})$ (%)	2.9
V (Å ³)	989.5(1)	Reflections collected	5115
Sp. Gr.	$I2/a$	Unique reflections	1453
Z	2	No. of $ F_o > 4\sigma F$	1282
Abs. coeff. (mm^{-1})	20.48	Refinement method	Least-squares on F^2 ;
$D(\text{calc})$ (g/cm^3)	4.530		fixed weights \propto to $1/\sigma(F^2)$
$F(000)$	1240	Goodness of fit on F^2	1.044
		Final $R(\text{obs})$ (%)	2.4
		$R(\text{all data})$ (%)	2.9
		wR_2	5.5
		GoF	1.044

TABLE 2. CHEMICAL COMPOSITIONS (wt. %) AND UNIT FORMULAE (*apfu*) FOR ARSENIOPLEITE AND CARYINITE

	Arseniopleite				Caryinite		
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
As ₂ O	53.56	51.80	50.60	44.98	47.80	49.78	48.84
V ₂ O ₅	—	—	—	—	—	—	0.24
P ₂ O ₅	0.19	0.20	0.30	—	0.80	0.19	0.95
Fe ₂ O ₃	3.33	3.50	0.50	3.68	—	—	—
FeO	—	—	—	—	0.50	0.54	0.10
MnO	24.35	26.30	20.10	28.25	19.10	18.66	17.90
MgO	3.29	2.50	7.10	3.10	3.10	3.09	3.24
CaO	5.91	6.10	7.40	8.11	10.80	12.12	10.82
PbO	2.22	3.30	8.70	4.48	11.50	9.21	12.73
BaO	0.24	0.20	0.30	—	0.80	1.03	0.17
Na ₂ O	5.89	5.53	5.00	—	4.18	5.16	4.82
TOTAL	98.96	99.40	100.20	98.27	98.58	100.68	99.81
As ⁵⁺	2.98	2.93	2.87	2.78	2.87	2.91	2.89
P	0.02	0.02	0.05	—	0.08	0.02	0.09
V ⁵⁺	—	—	—	—	—	—	0.02
Σ	3.00	2.95	2.92	2.78	2.95	2.93	3.00
Fe ³⁺	0.27	0.29	0.04	0.33	—	—	—
Fe ²⁺	—	—	—	—	0.19	0.05	0.01
Mn ²⁺	2.19	2.41	1.85	2.83	1.86	1.77	1.71
Mg	0.52	0.40	1.15	0.55	0.53	0.52	0.54
Ca	—	—	—	—	0.42	0.66	0.74
	2.98	3.10	3.04	3.71	3.00	3.00	3.00
Pb ²⁺	0.06	0.10	0.26	0.14	0.36	0.28	0.39
Ba	0.01	0.01	0.01	—	0.04	0.05	0.01
Ca	0.67	0.71	0.86	1.03	0.91	0.79	0.57
Na	1.21	1.16	1.05	—	0.94	1.12	1.04
	1.95	1.98	2.18	2.00	2.25	2.24	2.01

(1) This study; (2) Dunn & Peacor (1987), #85101, Sjö Mine; (3) Dunn & Peacor (1987), #151505, Långban; (4) Igelström (1888), with 5.67% H₂O; (5) Dunn & Peacor (1987), #139144, Långban; (6) Sjögren (1895), includes 0.40 K₂O and 0.53% H₂O; (7) Ercit (1993)
 — (below detection limit)

with only a few weak reflections violating *C*-centering. Fisher (1958) gave *C2/c* as the space group of alluaudite, Moore (1971) solved the crystal structure of alluaudite in *C2/c*, and this cell orientation has been used since by Moore & Ito (1978) and Dunn & Peacor (1987). Conversely, Strunz (1960) and Fisher (1962) used a cell orientation that is in accord with the (equivalent) space group *I2/a*, citing the smaller β angle ($\sim 99^\circ$ in *I2/a* versus $\sim 114^\circ$ in *C2/c*) as the reason for this choice of cell. Another important factor in this issue of orientation is the principal cleavage in these structures. If the *I2/a* orientation is used, the principal cleavage is {001}, whereas if the *C2/c* orientation is used, the principal cleavage is {101} (Fisher 1956). Ercit *et al.* (1986b) considered this issue when describing bobfergusonite (see in particular their Fig.1). They showed that adopting the *I*-centered orientation for the alluaudite structure is conformable with the space group *P2₁/c* for the wyllieite structure, and *P2₁/n* for the bobfergusonite structure (Ercit *et al.* 1986a, b). Alternatively, one could

adopt the *C2/c* orientation in alluaudite, and then wyllieite and bobfergusonite would become *P2₁/c* (Moore & Ito 1973, Moore & Molin-Case 1974, Fransolet 1995) and *P2₁/n*, respectively, the latter with its *a* and *c* axes reversed relative to those of Ercit *et al.* (1986a, b). Ercit (1993) has subsequently refined the crystal structure of caryinite in the space group *I2/a*. Either situation is acceptable from a structural perspective. We have chosen to adopt the orientation of Ercit *et al.* (1986b), in which alluaudite-group structures have the space group *I2/a*, the smaller β angle and the simpler orientation of the cleavage.

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 coordinates of caryinite (Ercit 1993). The sum of the medium-sized divalent and trivalent cations in the unit formula is 2.98 *apfu* (atoms per formula unit), and the sum of the large monovalent and divalent cations is 1.96 *apfu*. These sums are in accord with (Mn + Mg + Fe) ordered at the *M*(1) and *M*(2) sites, and (Na + Ca + Ba + Pb) ordered at the *X*(1) and *X*(2) sites. Accordingly, the *M*(1) and *M*(2) sites were considered as fully occupied by Mn and Mg, and the *X*(1) and *X*(2) sites were considered as fully occupied by Ca and Na at the start of the refinement. Full-matrix least-squares refinement of all positional, anisotropic-displacement and site-occupancy variables converged to an *R*₁ index of 2.3%. The small amounts of Pb and Ba (Table 2) were assigned to the *X*(2) site on the basis of ionic radius, and the refinement proceeded with no change in *R*₁ index. At this stage, some of the anisotropic-displacement parameters at the *X*(1) and *X*(2) sites were anomalously large. This feature was noted for *X*(1) but not *X*(2) in caryinite by Ercit (1993), and he introduced a model involving displacement of the *X*(1) site off its special position, causing a change in coordination number at this site. Using a displaced model for *X*(1) produces results similar to those of Ercit (1993), but when a displaced model was used for the *X*(2) site, it refined back onto the special position. Thus our final model is the same as that of Ercit (1993) for caryinite. Refined coordinates and anisotropic-displacement factors are listed in Table 3, selected interatomic distances are given in Table 4, and site-scattering values and assigned site-populations are given in Table 5. 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.

DESCRIPTION OF THE STRUCTURE

Arseniopleite is isostructural with alluaudite (Moore 1971) and caryinite (Ercit 1993); the general features of the structure are shown in Figure 1. There are two *M* sites, each coordinated by six O-atoms in an octahedral arrangement, with $\langle M-O \rangle$ distances of 2.218 and 2.129

TABLE 3. ATOM POSITIONS AND DISPLACEMENT FACTORS FOR ARSENIOPLEITE

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
X(1)	0.0217(3)	0.00131(16)	0.51196(17)	0.0127(4)	—	—	—	—	—	—
X(2)	1/4	0.01816(11)	0	0.0267(5)	0.0187(7)	0.0447(9)	0.0176(7)	0	0.0055(5)	0
M(1)	1/4	0.73506(5)	0	0.01148(20)	0.0108(3)	0.0119(3)	0.0114(3)	0	0.00108(22)	0
M(2)	0.08846(7)	0.15590(4)	0.21656(4)	0.01132(17)	0.0095(3)	0.0130(3)	0.0115(3)	0.00017(16)	0.00176(18)	-0.00058(17)
As(1)	1/4	0.28829(3)	0	0.01037(10)	0.01044(20)	0.00991(19)	0.01185(19)	0	0.00496(14)	0
As(2)	0.10766(4)	0.88811(2)	0.23133(2)	0.00967(9)	0.00892(15)	0.01111(15)	0.00956(14)	0.00024(9)	0.00322(10)	0.00053(10)
O(1)	0.0669(3)	0.21526(16)	0.03833(18)	0.0148(4)	0.011(10)	0.0196(10)	0.0148(10)	0.0018(8)	0.0044(8)	-0.0025(8)
O(2)	0.1481(4)	0.12546(18)	0.39581(20)	0.0245(5)	0.0408(15)	0.0166(11)	0.0179(11)	-0.0052(9)	0.0099(10)	-0.0145(10)
O(3)	0.2771(3)	0.83036(16)	0.16070(18)	0.0143(4)	0.0110(10)	0.0175(10)	0.0157(10)	-0.0032(8)	0.0061(8)	0.0007(8)
O(4)	0.1963(3)	0.90301(16)	0.37980(19)	0.0150(4)	0.0192(11)	0.0148(10)	0.0104(9)	-0.0008(7)	0.0011(8)	0.0016(8)
O(5)	0.1019(3)	0.31791(17)	0.28168(19)	0.0153(4)	0.0096(10)	0.0191(10)	0.0174(10)	0.0013(8)	0.0032(8)	0.0025(8)
O(6)	0.0552(3)	0.00113(16)	0.16087(19)	0.0160(4)	0.0189(11)	0.0135(10)	0.0156(10)	0.0039(8)	0.0030(8)	0.0036(8)

Å, respectively. The refined site-scattering values at the *M*(1) and *M*(2) sites are 24.8(1) and 44.0(2) *epfu* (electrons per formula unit), respectively, and the total site-scattering, 68.8 *epfu*, is in close agreement with the effective scattering of (Mn + Mg + Fe) in the unit formula (Table 2): 68.0 *epfu*. The refined site-scattering at *M*(1) is in accord with complete occupancy of this site by Mn²⁺, and the site-population was assigned as such (Table 5). The remaining Mn, together with the Mg and Fe in the unit formula, were assigned to the *M*(2) site, and the resulting calculated site-scattering value of 43.5 *epfu* is in close agreement with the refined site-scattering value of 44.0(2) *epfu* at *M*(2). We may calculate the expected mean bond-lengths from the assigned site-populations using the hard-sphere model and the ionic radii of Shannon (1976). For the *M*(1) site, <*M*(1)–O>(calc) is equal to 1.38 + 0.83 = 2.21 Å, in very close agreement with the observed value of 2.218 Å (Table 4). For the *M*(2) site, <*M*(2)–O> is equal to 1.373 + 0.776 (with Fe³⁺) or 0.795 (with Fe²⁺) = 2.149 (Fe³⁺) or 2.168 (Fe²⁺); the observed value is 2.128 Å (Table 4). The resulting differences are 0.020 (Fe³⁺) and 0.039 (Fe²⁺) Å, respectively; these values favor the assignment of Fe to the trivalent state, although the difference of 0.02 Å for this assignment is still significantly larger than that observed at the *M*(1) site (Table 5). However, if similar calculations are done for caryinite (Ercit 1993), the corresponding differences in the observed and calculated <*M*–O> distances are 0.009 and 0.020 Å, respectively, for the *M*(1) and *M*(2) sites. As these values are exactly the same as are observed in arsenioleite (and caryinite has insignificant Fe and hence no valence-assignment problem), this agreement suggests that the assigned site-populations of Table 5 are valid. The sums of the incident bond-valence at the *M*(1) and *M*(2) sites are in accord with this assignment. The aggregate formal charges at the *M*(1) and *M*(2) sites are 2.0⁺ and

2.14⁺, respectively, and the analogous bond-valence sums are 1.86 and 2.22 *vu* (Table 6).

There are two *X* sites, each surrounded by eight atoms of oxygen, and each having a wide dispersion of *X*–O distances. The *X*(1) site is actually displaced off the 4*b* position, and only one of the two adjacent *X*(1) sites is occupied in any local configuration. The *X*(1) cation is displaced toward one O(2) atom and away from the symmetrically equivalent O(2) atom (as is also the case in caryinite, Ercit 1993), and the *X*(1) site is actually [7]-coordinated (Table 4). Similar anisotropy is shown for the *X*(1) site in nickenichite (Auernhammer *et al.* 1993) and the synthetic alluaudite-like phosphates Na Mn Fe₂ (PO₄)₃ and (Na_{0.5}Li_{0.5}) Mn Fe₂ (PO₄)₃ (Hatert *et al.* 2000), although these authors chose not to split the *X*(1) site in their refinements. Note that all of these structures also show exaggerated anisotropic displacements for the *X*(2) site, although they are not always as large as that for the *X*(1) site, and we were unable to satisfactorily refine the structure of arsenioleite with a split model for the *X*(2) site. Summing the constituent ionic radii gives 1.376 + 1.079 = 2.46 Å, compared with the observed value of 2.51 Å (Table 4). By analogy with caryinite and alluaudite, all Ca is assigned to the *X*(1) site, and the refined site-scattering value of 17.5 *epfu* indicates that the balance of the site population is made up by Na. The remaining Na, Pb and Ba is thus assigned to the *X*(2) site, and the resulting calculated site-scattering value of 15.7 *epfu* is in exact agreement with the refined site-scattering value, 15.8(2) *epfu* (Table 5). Summing the constituent ionic radii at *X*(2) gives 1.380 + 1.189 = 2.57 Å, compared with the observed value of 2.73 Å (Table 4). The differences between the observed and calculated <*X*–O> distances are large, but similar differences also occur in caryinite (Ercit 1993) and seem to be characteristic of this structure type. The sums of the incident bond-valences at the

X(1) and X(2) sites are in accord with the assigned site-populations. The aggregate formal charges at X(1) and X(2) are 1.68⁺ and 1.07⁺, respectively, and the analogous bond-valences sums are 1.52 and 1.00 *vu* (Table 6).

End-member composition and the status of arseniopleite

As noted above, there has been some question in the literature as to the validity of arseniopleite, and its status as a distinct species has been questioned (Nystén *et al.* 1999). Hawthorne (2002) has emphasized the importance of considering end-member compositions when dealing with questions of species status, particularly where the minerals in question involve complicated schemes of solid solution and site ordering. Inspection of Table 5 shows that Ca is dominant at X(1), Na is dominant at X(2), and Mn²⁺ is dominant at both M(1)

and M(2), and hence the end-member formula can be written as shown in Table 7. A similar procedure for caryinite, using the site-occupancies of Ercit (1993), gives the end-member formula in Table 7. As suggested by Dunn & Peacor (1987) and Ercit (1993), arseniopleite is distinct from caryinite by the presence of dominant Mn²⁺ rather than Ca (as in caryinite) at the M(1) site.

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TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN ARSENIOPLEITE

M(1)–O(1)a	x2	2.221(2)	X(2)–O(1)	x2	2.922(3)
M(1)–O(3)	x2	2.184(2)	X(2)–O(3)e	x2	3.037(2)
M(1)–O(4)	x2	<u>2.247(2)</u>	X(2)–O(6)f	x2	2.521(2)
<M(1)–O>		2.217	X(2)–O(6)	x2	<u>2.447(2)</u>
			<X(2)–O>		2.732
M(2)–O(1)		2.142(2)			
M(2)–O(2)		2.037(2)	As(2)–O(3)		1.693(2)
M(2)–O(3)c		2.110(2)	As(2)–O(4)		1.693(2)
M(2)–O(5)		2.234(2)	As(2)–O(5)b		1.680(2)
M(2)–O(5)d		2.133(2)	As(2)–O(6)g		<u>1.683(2)</u>
M(2)–O(6)		<u>2.114(2)</u>	<As(2)–O>		1.687
<M(2)–O>		2.128			
			As(1)–O(1)	x2	1.686(2)
X(1)–O(2)		2.344(3)	As(1)–O(2)d	x2	<u>1.687(2)</u>
X(1)–O(2)h		2.365(3)	<As(1)–O>		1.687
X(1)–O(2)i		2.816(3)			
X(1)–O(4)j		2.431(3)			
X(1)–O(4)e		2.435(3)			
X(1)–O(4)k		2.449(3)			
X(1)–O(4)c		<u>2.744(3)</u>			
<X(1)–O>		2.512			

a: $x+\frac{1}{2}, -y+1, z$; b: $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; c: $x-\frac{1}{2}, -y+1, z$; d: $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; e: $x, y-1, z$; f: $x+\frac{1}{2}, -y, z$; g: $x, y+1, z$; h: $-x, -y, -z+1$; i: $-x+\frac{1}{2}, y, -z+1$; j: $-x, -y+1, -z+1$; k: $-x+\frac{1}{2}, y-1, -z+1$

TABLE 6. BOND-VALENCE TABLE * (*vu*) FOR ARSENIOPLEITE

	X(1)	X(2)	M(1)	M(2)	As(1)	As(2)	Σ
O(1)		0.084 ² ₁	0.306 ² ₁	0.353	1.236 ² ₁		1.979
O(2)	0.290 ³ ₁ – 0.277 ³ ₁ – 0.113			0.462	1.231 ² ₁		1.977
O(3)		0.071 ² ₁	0.337 ² ₁	0.382		1.205	1.995
O(4)	0.240 ³ ₁ – 0.239 ³ ₁ – 0.232 ³ ₁ – 0.130 ³ ₁ –		0.287 ² ₁			1.205	1.906
O(5)				0.283		1.263	1.907
				0.361			
O(6)		0.162 ² ₁		0.380		1.249	1.976
		0.185 ² ₁					
Σ	1.521	1.004	1.860	2.221	4.934	4.922	

* calculated from the curves of Brown (1981)

TABLE 7. END-MEMBER COMPOSITIONS (*apfu*) FOR ARSENIOPLEITE AND CARYINITE

X(1)	X(2)	M(1)	M(2) ₂	Mineral	
Ca	Na	Mn ²⁺	Mn ²⁺ ₂	As ₃ O ₁₂	Arseniopleite
Ca	Na	Ca	Mn ²⁺ ₂	As ₃ O ₁₂	Caryinite

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

	RSS	<M,X–O>	Site-populations	CSS	<M,X–O> _{calc}
M(1)	24.8(1)	2.218	1.00 Mn ²⁺	25	2.21
M(2)	44.0(2)	2.129	1.21 Mn ²⁺ + 0.52 Mg + 0.27 Fe ³⁺	43.5	2.16
X(1)	17.5(2)	2.512	0.68 Ca + 0.32 Na	17.1	2.46
X(2)	15.8(2)	2.732	0.93 Na + 0.06 Pb ²⁺ + 0.01 Ba	15.7	2.57

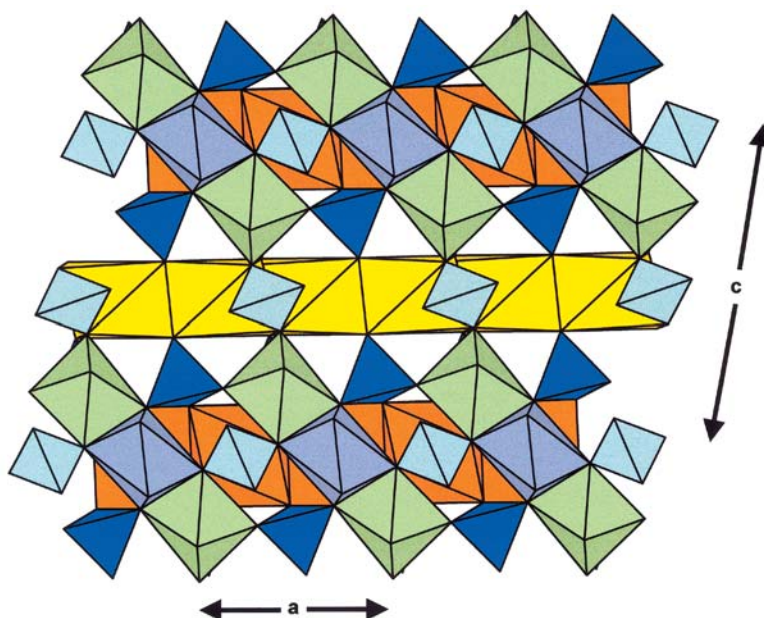


FIG. 1. The crystal structure of arseniopleite projected down [010]; pale blue: As(1) tetrahedra; dark blue: As(2) tetrahedra; intermediate blue: $M(1)$ octahedra; green: $M(2)$ octahedra; yellow: $X(1)$ polyhedra; orange: $X(2)$ polyhedra.

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