

New data on the relation between caryinite and arsenioleite

PETE J. DUNN

Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, USA

AND

DONALD R. PEACOR

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, USA

Abstract

Caryinite from Långban, Sweden, and arsenioleite from both the Långban and Sjö Mines in Sweden, are re-examined chemically and crystallographically. Both species are monoclinic, with space group $C2/c$, and similar lattice parameters. The general formula for caryinite is $\text{Na}_4\text{Ca}_4\text{Ca}_4(\text{Mn,Mg})_8(\text{AsO}_4)_{12}$, and that for arsenioleite is $\text{Na}_4\text{Ca}_4\text{Mn}_4(\text{Mn,Mg})_8(\text{AsO}_4)_{12}$. The species status of arsenioleite remains uncertain; it may have Mn dominant in the $M(1)$ site.

KEYWORDS: caryinite, arsenioleite, arsenates, Långban, Sjö mines, Sweden.

Introduction

CARYINITE and arsenioleite have been known to have the same basic structure, but have been characterized as having related but different compositions, especially in the relative proportions of Pb, Na, and Ca/Mn (Moore, 1968, 1971). Although considered to be closely related to alluaudites, they were understood to contain water, with substantial differences in their water contents (Sjögren, 1895, Igelström, 1888). Additionally, their X-ray diffraction powder patterns, although similar, show differences in both the presence and intensity of some reflections. Moore (1968) proposed that they are the same species, although good analytical data for each was lacking. Accordingly, we investigated these minerals using single-crystal X-ray diffraction and microprobe analytical procedures to provide modern analyses and crystallographic data.

Caryinite

Caryinite, known only from Långban, Sweden, was originally described by Lundström (1874) on the basis of an analysis which was of impure material. The definition of this species, based on an analysis by Mauzelius in Sjögren (1895), has been the subject of a number of investigations in the older literature, summarized by Boström (1957),

and Hintze (1922). The unit cell was defined by Boström (1957), who suggested a structural relation to the closely associated berzeliite. The isostructural relation of caryinite and alluaudite was noted by Strunz (1960), Moore (1968), and confirmed by Moore (1971).

The samples utilized in the present study were all from Museum collections and verified as caryinite by comparison with the X-ray powder data of Boström (1957), obtained from the original material. The data for our samples are in excellent agreement with this published data. In our samples, caryinite occurs associated with a variety of minerals including rhodonite, calcite, diopside (schefferite), adelite, hausmannite, and especially berzeliite. Most caryinite samples examined in this study contained some intimately admixed berzeliite; this was very likely a contaminant in older analyses and might have contributed the small amount of Si reported by Boström (1957). Care was taken to obtain uncontaminated material for our density determinations by splitting crystals along one or more good cleavages, by optical examination, and by subsequently dissolving portions of the crystals used for density determinations in HCl, whereupon caryinite dissolves slowly and any berzeliite contaminants remain, due to lower solubility. No such contaminants were found in the crystals we utilized;

the density determinations, performed on clean fragments, employing a Berman balance and temperature correction, yielded the value 4.37 g/cm^3 for sample #139144.

Arseniopleite

Arseniopleite was originally described by Igelström (1888) from the Sjö Mine, near Grythyttan, Örebro, Sweden. It was re-examined by Moore (1968) who, on the basis of single-crystal studies, proposed that arseniopleite and caryinite were identical. Caryinite, however, was still known as a water-containing phase, and the chemistry of these minerals had not been re-examined. Furthermore, the conclusions of Moore (1968) were based only on rotating crystal and powder photographs. Although these data clearly established the basic isotypic relation, the relation was ambiguous in detail because:

(1) the space group of caryinite (Boström, 1957) was determined as $P2_1/c$ (rather than $I2/c$, the space group of alluaudite-type structures) on the basis of only a few very weak I -centering-violating reflections, and

(2) the unit cell of arseniopleite was determined by methods which could not discriminate between such subtle features, leaving some doubt that arseniopleite and caryinite have the same space group.

Nevertheless, the data summarized by Moore led him to propose that these minerals are the same species. The data of this paper support a close relation, albeit with more specific data, but leave arseniopleite as a possibly valid species.

The samples of arseniopleite utilized in the present study were all confirmed as arseniopleite on the basis of excellent agreement of their powder data with those of Moore (1968). After checking for included contaminants as was done for caryinite, the density was determined to be 4.22 g/cm^3 for sample #85101. The Sjö Mine samples of arseniopleite used in this study are associated predominantly with calcite and rhodonite, with lesser amounts of other phases. Arseniopleite is frequently rimmed by a dark blue-violet mineral which gives the X-ray powder pattern of sarkinite. During the course of our investigation, we also obtained two samples from Långban which yielded powder data in excellent agreement with those for arseniopleite. These similarly occur in calcite-dominant rocks: #151505 as brown irregular seams and fracture-fillings; and #149824 as grey crystals, lenticular in exposed cross-section, associated with calcite and berzeliite, with a typical metamorphic texture.

X-ray crystallography

Both arseniopleite (#85101) and caryinite (#139144) were studied using the Weissenberg method. Both were found to give diffraction data consistent with the unit cell and space group as determined by Boström (1957), further verifying that they are isostructural with alluaudite, but with one exception. Boström noted that six reflections present on zero-level c -axis photographs of caryinite violated the C -centering rule. Photographs of caryinite were therefore deliberately overexposed in this study, but no such C -centering-violating reflections were observed. The space group of our crystals is therefore $C2/c$, in part by analogy with alluaudite (Moore, 1971). We have no explanation as to why different crystals should apparently display different diffraction relations.

Significant differences in intensity and spacing of some reflections with large d -values were observed between powder photographs of caryinite and arseniopleite, especially for 020 and 110, and it was these differences, in part, which led us to suspect that these minerals might be different species. However, observation of single-crystal patterns shows that the intensity differences were duplicated there, as consistent with the same space group ($C2/c$). However, there is a general similarity in the intensities of equivalent reflections of both species. We ascribe the differences to variations in solid solution.

Chemical composition

The samples studied were analysed utilizing an ARL-SEM-Q electron microprobe with operating conditions: 15 kV, $0.025 \mu\text{A}$; corrections by a modified version of the MAGIC-4 program; standards used were PbO (Pb), manganite (Mn), baryte (Ba), fluorapatite (P), synthetic olivenite (As), and hornblende (Fe, Mg, Ca). Microchemical tests gave a strong to moderate positive reaction for ferric iron in arseniopleite, and an inconclusive reaction for ferric or ferrous iron in caryinite. Samples 85101 and 139144, found to be free of contaminants, were subjected to water determinations using the Penfield method. Both samples are essentially anhydrous; the results were (85101: $0.01\% \text{H}_2\text{O}^-$, $0.05\% \text{H}_2\text{O}^+$) (139144: $0.1\% \text{H}_2\text{O}^-$, $0.05\% \text{H}_2\text{O}^+$). The oxidation state of As is given as pentavalent based on determinations in the previously cited literature, and the results of microchemical tests we performed on arseniopleite (85101). The same test could not be performed on caryinite due to interference from the high Pb-content. The resultant analyses are presented in Table 1, together with the original analyses of these phases. We consider

TABLE 1. Analyses of caryinite and arseniopleite

	Caryinite, Långban		Arseniopleite, Sjö		Arseniopleite, Långban
	#139144	Sjögren*	#85101	Igelström**	151505
Fe ₂ O ₃	0.0%	n.g.	3.5%	3.68%	0.5
FeO	0.5	0.54%	0.0	n.g.	0.0
MgO	3.1	3.09	2.5	3.10	7.1
CaO	10.8	12.12	6.1	8.11	7.4
MnO	19.1	18.66	26.3	28.25	20.1
PbO	11.5	9.21	3.3	4.48	8.7
BaO	0.8	1.03	0.2	n.g.	0.3
P ₂ O ₅	0.8	0.19	0.2	n.g.	0.5
As ₂ O ₅	47.8	49.78	51.8	44.98	50.6
Na ₂ O	4.18#	5.16	5.53#	n.g.	5.0
Total	98.6	100.68	99.4	98.27	100.2
<u>Cations per 48 oxygens</u>					
Fe ³⁺	0.00		1.14		0.16***
Fe ²⁺	0.19		0.00		0.00
Mg	2.12		1.61		4.60
Ca	5.32		2.83		3.45
Mn	7.44		9.64		7.39
Pb	1.42		0.38		1.02
Ba	0.14		0.03		0.05
P	0.31		0.07		0.18
As	11.49		11.72		11.48
Na	3.74		4.65		4.20
<u>Ranges of compositions for additional samples</u>					
Fe ₂ O ₃	0		3.2 - 3.7		0.0 - 0.5
FeO	0.4 - 0.8		0		0
MgO	3.0 - 4.3		2.5 - 4.4		7.1 - 8.0
CaO	9.2 - 11.8		5.9 - 6.5		7.4 - 7.7
MnO	18.6 - 20.4		24.9 - 26.4		20.1 - 21.5
PbO	9.2 - 12.9		1.3 - 3.5		3.5 - 8.7
BaO	0.0 - 1.1		0.2 - 0.4		0.0 - 3.7
P ₂ O ₅	0.8 - 1.6		0.2 - 0.5		n.d.
As ₂ O ₅	47.1 - 50.5		50.1 - 53.7		50.6 - 52.4
Na ₂ O	4.2 - 5.2		5.5 - 6.4		4.8 - 5.0

* ---Sjögren (1895), includes 0.53% H₂O, 0.37% K₂O.**---Igelström (1888), includes 5.67% H₂O, traces of Sb₂O₅ and Cl.

***--Oxidation state of Fe not determined.

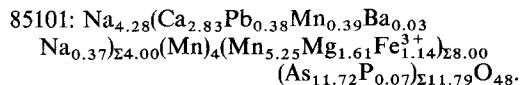
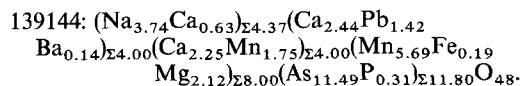
-determined by flame emission, after decomposition with HF-H₂SO₄.

n.g. = not given.

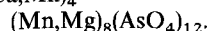
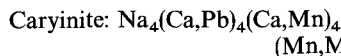
these analyses to be of slightly lower precision than usual because of the lack of suitable control standards to use for checking the corrections for Na and Pb.

Examination of the analytical data permit a number of observations. Caryinites are much richer in Pb and Ca than arseniopleite. Na concentrations are inversely proportional to those of Pb in general, and Fe is almost wholly ferric in arseniopleite. Calculations of empirical compositions, based on 48 oxygen atoms in conformity with the alluaudite structure, adopting the site assignments suggested by Moore (1971), and based on the site geometries and charge balance requirements of the alluaudite structure, yield for samples 139144 (caryinite) and

85101 (arseniopleite), respectively, for X(2), X(1), M(1), and M(2):



These formulae imply the idealized formulae for caryinite and arseniopleite to be:



Moore and Molin-Case (1974) determined the complex ordering scheme in wylleite, which has a structure that is an ordered derivative of that of alluaudite. Because Boström (1957) had observed reflections in diffraction patterns of caryinite that apparently caused a decrease in symmetry as had been observed for wylleite, Moore and Molin-Case suggested a modified cation ordering scheme based on the cation polyhedron geometries of wylleite. Because no such reflections were observed in diffraction patterns of caryinite in this study, we prefer the above ordering scheme as consistent with the suggestions of Moore (1971) based on the cation polyhedron geometries of alluaudite. However, both cation distributions are quite similar, differing primarily only in an interchange of Pb and some Na in the X(1) and X(2) sites.

Arseniopleite status

In the absence of a crystal structure determination, giving precise site occupancies in these alluaudite-group minerals, we propose that arseniopleite be considered a valid species pending a definitive resolution of its identity with caryinite. If the cation assignments follow the scheme proposed by Moore for alluaudite, then the above given formulae 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. Until this is established, we consider arseniopleite to be closely related to, but not identical with, caryinite.

Much as in the related alluaudite phosphate structures, there are serious nomenclature concerns to be considered. There is little benefit to science in naming *all* the possible end-members of this series, inasmuch as X(1), X(2), M(1), and M(2) can all be occupied by different species, and X(1) and X(2) can be vacant. Arseniopleite, however, is already named and, because the data do imply (but not prove) that M(1) has different cations in caryinite and arsenio-

pleite, we urge that the name be *provisionally* retained until additional studies are done, or group nomenclature decisions are made for this structure type.

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