MORELANDITE, A NEW BARIUM ARSENATE CHLORIDE MEMBER OF THE APATITE GROUP

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ABSTRACT

Morelandite, $(Ba,Ca,Pb,Fe,Mn)_5[(As,P)O_4]_3Cl$ (ideally, $Ba_5(AsO_4)_3Cl$) occurs as small irregular masses associated with hausmannite and calcite from the Jakobsberg mine, near Nordmark, Sweden. The mineral is grey to light yellow with a white streak, greasy to vitreous lustre, density 5.33 g/cm³, hardness 4½, and cleavage poor on {001}. Optically, it is uniaxial (+) with ω 1.880 and ϵ 1.884. Morelandite is hexagonal, $P6_3$ or $P6_3/m$, a 10.169(2), c 7.315(2) Å. The strongest lines in the powder are (in Å): 5.089(3)(110), 4.175(3)(111), 3.658(5)(002), 3.030(10)(211), 2.969(7)(112), 2.935(6)(300) and 1.965(3)(213). Morelandite is a member of the apatite group and is closely related to mimetite, $Pb_5(AsO_4)_3Cl$, but without the monoclinic superstructure of the latter. Some degree of cation ordering is likely in the morelandite structure.

SOMMAIRE

On trouve la morelandite $(Ba,Ca,Pb,Fe,Mn)_5$ $[(As,P)O_4]_3Cl$ (formule idéale $Ba_5(AsO_4)_3Cl$) en petites masses irrégulières accompagnées de hausmannite et de calcite dans la mine de Jakobsberg, près de Nordmark (Suède). Ce minéral varie du gris au jaune pâle et possède une rayure blanche, un éclat gras à vitreux, une densité de 5.33, une dureté de 4½ et un clivage imparfait suivant {001}. La morelandite est uniaxe positive, ω 1.880, ϵ 1.884, et hexagonale, $P6_3$ ou $P6_3/m$, a 10.169(2), c 7.315(2)Å. Les raies les plus intenses du diagramme de poudre correspondent aux espacements suivants (en Å): 5.089(3)(110), 4.175(3)(111), 3.658(5)(002), 3.030(10)(211), 2.969(7)(112), 2.935(6)(300) et 1.965(3)(213). La morelandite, membre de la famille des apatites, est voisine de la mimétite, $Pb_5(AsO_4)_3Cl$, dont elle ne possède toutefois pas la surstructure monoclinique. On s'attend à trouver une distribution ordonnée des cations dans la structure.

(Traduit par la Rédaction)

INTRODUCTION

During a systematic analytical study of the chemical miscibility between mimetite and hedyphane, a specimen from the Jakobsberg mine in Sweden was found to contain a very large amount of barium. A detailed study of this specimen resulted in its characterization as a new mineral species belonging to the apatite group. The mineral has the ideal composition $Ba_5(AsO_4)_3Cl$, making it closely related to mimetite, $Pb_5(AsO_4)_3Cl$.

The mineral has been named for Grover C. Moreland, supervisor of the sample preparation laboratory at the Smithsonian Institution, in honor of his dedication to the support of mineralogical research. His devotion to excellence in workmanship has assisted innumerable scientists and we take special pleasure in honoring him in this manner. Both the mineral and the name were approved in advance of publication by the Commission on New Minerals and Mineral Names, I. M. A. Holotype material is deposited in the National Museum of Natural History, Smithsonian Institution, Washington, D.C. 20560 under catalog number C4147. Additional holotype material will be deposited in the British Museum (Nat. Hist.), London, England, The National Science Museum, Tokyo, Japan, The Royal Ontario Museum, Toronto, Ontario and the collection of the Geological Survey of Canada, Ottawa, Ontario.

LOCALITY, DESCRIPTION AND PHYSICAL PROPERTIES

Morelandite is known only from one specimen, originally from the Canfield collection, and now part of the Smithsonian mineral collection. The original label and catalog entry contain no additional locality information beyond the designation *Jakobsberg, Sweden*. The name Jakobsberg refers to a small mine about 1 km south of Nordmark, Sweden.

The specimen consists of a layer of densely packed hausmannite crystals varying in size

from microscopic to 1.0mm. The hausmannite is intermixed with calcite in a layering that suggests stratification. Calcite is present as a 2cm thick layer on top of the hausmannite in addition to being admixed with it. Morelandite occurs as irregular segregations within the calcite. No crystals were found and there appears to be no recognizable orientation between the calcite and the enclosed morelandite. An exposed surface of morelandite measures 2.5 × 1.0 cm and is somewhat lenticular in cross section.

Morelandite has a Mohs hardness of about 4½. The streak is white. The color of the mineral varies from light yellow to almost pure grey. The lustre of a fresh surface is greasy to vitreous. Cleavage is extremely weak parallel to {001}. The density, determined with a Berman balance in toluene and with a temperature correction, is 5.33 g/cm³; this compares with a calculated density of 5.30 g/cm³ from the given composition and unit-cell volume.

Optically, the mineral is uniaxial (+) with ω 1.880 and ϵ 1.884, both $\pm$ 0.004. Morelandite is completely soluble in cold dilute 1:1 nitric acid and whitens to an opaque chalky appearance after prolonged immersion in cold dilute 1:1 hydrochloric acid. The mineral does not respond to ultraviolet radiation.

COMPOSITION

All elements were determined using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a beam current of 0.15 μA. Standards used were barite for barium; manganite for manganese; synthetic PbO for lead; fluorapatite for calcium, phosphorus and fluorine; olivenite for arsenic; chlorapatite for chlorine; and hornblende for iron. The data were corrected for background, backscatter, absorption and fluorescence using the *MAGIC* program of The Geophysical Laboratory. A wavelength-dispersive microprobe scan indicated

TABLE 1. MICROPROBE ANALYSIS OF MORELANDITE

CaO*	8.85%	FeO	0.41%	BaO	33.00%
MnO	0.39	PbO	24.85	P_2O_5	2.05
As_2O_5	28.11	Cl	3.69	F	0.00
H_2O	tr	O≡Cl	0.83		
Sum	100.52				

* Accuracy of data ±3% relative for elements present in amounts exceeding 1.00 wt. %.

the absence of other detectable elements. The analysis given in Table 1 yields the following formula, calculated on the basis of the cell dimensions, density and normalization to 100%: $(Ba_{2.25}Ca_{1.65}Pb_{1.16}Fe_{0.06}Mn_{0.06})$ $[(AsO_4)_{2.56}(PO_4)_{0.30}]$ $Cl_{1.09}$.

The composition of morelandite resembles that of mimetite, to which it is crystallographically related. The *Baryt-hedyphane* of Vermin (Hey 1962) has been re-examined and found to be calcian barian mimetite with Pb > Ca or Ba (British Museum specimen # 53688).

CRYSTALLOGRAPHY

The chemical formula of morelandite suggests a mineral of the apatite group and this was confirmed by X-ray diffraction. Morelandite is hexagonal, $P6_3$ or $P6_3/m$ (probably the latter as this is the symmetry of hexagonal apatites), with a 10.169(2), c 7.315(2)Å, V 655.1(3)Å³ and c/a 0.7193. The unit cell and space group were determined from precession photographs and the cell parameters refined by least-squares using twelve reflections measured

TABLE 2. X-RAY POWDER DATA FOR MORELANDITE

I_{obs}	d_{obs}	d_{calc}	hkl	I_{obs}	d_{obs}	d_{calc}	hkl
2	8.86	8.81	100	<<1	1.663	1.664	420
<<1	5.625	5.627	101	<<1	1.651	1.651	331
3	5.089	5.085	110	<<1	1.621	1.623	421
<<1	4.406	4.403	200	<<1	1.601	1.603	214
3	4.175	4.175	111	1	1.585	{1.587	502
5	3.658	3.658	002			{1.582	510
2	3.335	3.329	210			{1.556	323
10	3.030	3.030	211	2b	1.551	{1.552	304
7	2.969	2.969	112			{1.546	511
6	2.935	2.935	300	<1	1.515	1.515	422
1	2.460	2.462	212	<<1	1.451	1.452	512
<1	2.317	2.317	311	<<1	1.408	{1.407	404
2	2.200	{2.202	400			{1.406	115
		{2.199	113	<<1	1.386	{1.388	205
1	2.086	2.087	222			{1.385	521
<1	2.024	{2.031	312	<<1	1.361	1.362	602
		{2.020	320	1	1.340	{1.343	610
3	1.965	1.967	213			{1.339	215
2	1.946	1.947	321	1	1.325	{1.327	513
<1	1.919	1.922	410			{1.325	414
1	1.887	1.886	402	<<1	1.271	{1.271	440
<1	1.827	1.829	004			{1.269	504
<1	1.764	{1.768	322	<<1	1.258	1.258	530,700,603
		{1.761	500	<<1	1.231	1.231	424
		{1.760	223	<<1	1.220	{1.221	620,523
<<1	1.725	1.726	313			{1.219	006,405

b = broad line

114.6 mm Debye-Scherrer camera, NBS silicon internal standard, CuKα radiation, visually estimated intensities

from a Debye-Scherrer photograph taken with $CuK\alpha$ radiation and an NBS silicon (a 5.43008Å) internal standard. The X-ray powder diffraction data for morelandite are given in Table 2. As compounds with the apatite structure may be monoclinic-pseudohexagonal, the precession photographs were deliberately overexposed using unfiltered $MoK\alpha$ radiation, but no monoclinic superstructure reflections were observed.

DISCUSSION

The ideal composition of morelandite is $Ba_5(AsO_4)_3Cl$, but a comparison of its cell parameters with those of pure synthetic calcium, lead and barium arsenate chlorides (Kreidler & Hummel 1970) suggests extensive substitution of Ca and Pb for Ba in the natural specimen:

	a	c	V
$Ca_5(AsO_4)_3Cl$	10.04Å	6.83Å	596Å^3
Morelandite	10.17	7.32	655
$Pb_5(AsO_4)_3Cl$	10.24	7.44	676
$Ba_5(AsO_4)_3Cl$	10.54	7.73	744

The hexagonal apatite structure contains two nonequivalent cation positions: a larger nine-coordinated $M(1)$ position of multiplicity four and a smaller seven-coordinated $M(2)$ position of multiplicity six. There is experimental evidence, summarized by Urusov & Khudolozhkin (1975), for ordering of cations in these two positions. Specifically, Be, Mg, Fe, and Mn prefer the $M(1)$ sites whereas Ba and Sr prefer the $M(2)$ sites, the opposite of what one would expect from the ionic radii of these elements. Urusov & Khudolozhkin propose that the $M(1)$–ligand bonds are more covalent than the $M(2)$–ligand bonds, which causes atoms more electronegative than calcium to prefer the $M(1)$ sites and those less electronegative than calcium to prefer the $M(2)$ sites. The influence of electronegativity predominates over that of ionic size. If this explanation is correct, lead, having both a high electronegativity relative to calcium and a large ionic radius, should have a strong affinity for $M(1)$.

Unfortunately, experimental confirmation of this prediction is lacking and several possible ordering schemes may be constructed for morelandite using the available site-preference information. For example, if Ba were completely ordered in $M(2)$ and Pb, Fe and Mn completely ordered in $M(1)$ with the Ca distributed between the two positions to make six and four atoms,

respectively, the resulting distribution would be $(Ba_{4.34}Ca_{1.66})_{\Sigma6}(Pb_{2.25}Ca_{1.52}Fe_{0.12}Mn_{0.11})_{\Sigma4}$. Here the number of cations has been normalized to 10 from the analytical value of 10.36. Regardless of what the actual distribution may be, some degree of cation ordering is likely to occur in morelandite.

At room temperature stoichiometric (or nearly stoichiometric) chlorapatite, $Ca_5(PO_4)_3Cl$, is monoclinic-pseudohexagonal with space group $P2_1/b$ (Mackie et al. 1972). However, a statistically hexagonal ($P6_3/m$) chlorapatite can exist at this temperature due to positional disorder of the chlorine atoms, a situation promoted by the presence of vacancies or substituent atoms on some of the chlorine sites. Above about 200°C, hexagonal chlorapatite is the stable form (Prener 1967). On the other hand, stoichiometric strontium chlorapatite, $Sr_5(PO_4)_3Cl$, (Sudarsanan & Young 1974) conforms strictly to $P6_3/m$ symmetry at room temperature. In morelandite, repeated and very careful chemical analyses for chlorine seem to rule out any vacancies or substitutions for this element. It would therefore seem that morelandite, like strontium chlorapatite, is strictly hexagonal and for the same reason. Keppler (1968, 1969) states that mimetite has the $P2_1/b$ superstructure of monoclinic apatites, with the transformation to the hexagonal form occurring at about 100°C. He does not cite chemical analyses for his samples; hence, the possible role of nonstoichiometry and ionic substitutions cannot be evaluated for this mineral.

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