Hedyphane from Franklin, New Jersey and Långban, Sweden: cation ordering in an arsenate apatite[1]

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Abstract

Hedyphane, traditionally formulated as $(Ca,Pb)_5(AsO_4,PO_4)_3Cl$, is redefined as $Ca_2Pb_3(AsO_4)_3Cl$ with $Z = 2$. The space group is $P6_3/m$ with $a = 10.140(3)$ and $c = 7.185(4)$Å. Observed and calculated densities are 5.85 and 5.99 g/cm^3, respectively. The crystal structure has been refined to residuals of 0.062 (weighted) and 0.076 (unweighted) using 550 reflections. Ordering of Ca and Pb on equipoints $4f$ and $6h$, respectively, is complete except for a possible minor amount of solid solution (ca. 1%). Cation ordering in hedyphane is attributed to a preference by atoms with sterically active electron lone pairs, e.g., Pb(II), for the asymmetrically coordinated $6h$ site. A study of minerals in the solid solution series $Ca_xPb_{5-x}(AsO_4)_3Cl$ from Långban, Sweden, and Franklin, New Jersey, reveals a lack of compositions in the range $2.3 \le x \le 4.8$, implying a miscibility gap in this region.

Introduction

In the course of a systematic study of lead calcium arsenate apatites from Franklin, New Jersey, and Långban, Sweden, two salient features appeared upon tabulation of the chemical analyses. These features, a clustering of analyses near the ratio Pb:Ca = 3:2 and a conspicuous lack of compositions in one region along the $Pb_5(AsO_4)_3Cl–Ca_5(AsO_4)_3Cl$ join, suggested that additional study was warranted. The results of this investigation, in particular an analysis of the crystal structure of hedyphane, have resulted in a redefinition of this mineral, which has heretofore held a rather ambiguous position within the apatite group. The data also permit some definition of the possible limits of solid solution in the system $Pb_5(AsO_4)_3Cl–Ca_5(AsO_4)_3Cl$.

The general formula for the hexagonal ($P6_3/m$) apatites may be written $A_4B_6(XO_4)_6Z_2$ in recognition of the fact that the structure contains two symmetrically nonequiva-

lent cation sites. The A site corresponds to equipoint $4f$ and is coordinated by nine oxygen atoms at the vertices of a distorted tricapped trigonal prism, whereas the B site corresponds to equipoint $6h$ with a coordination number which depends on the identity of Z. That is, B is coordinated by six oxygen and one Z atom when Z = F or OH and by six oxygen and two Z atoms when Z = Cl, Br, or I. (The cadmium apatites are exceptions to this rule (Sudarsanan et al., 1977)).

The segregation of cations onto two nonequivalent sites creates a potential for ordering in mixed-cation apatites, the simplest possible ordering scheme being A_4B_6. While numerous apatites, both natural and synthetic, exist with this 4:6 ratio (Roy et al., 1978), very few have been subjected to crystal structure analysis to verify the ordering implicit in their formulas. Moreover, such studies as have been made have often relied upon powder X-ray diffraction data to deduce the presence or absence of ordering. In this paper we present a crystal structure analysis based on single-crystal data to demonstrate cation ordering of the 4:6 type in hedyphane.

Nomenclature

Hedyphane was originally described from the type locality, Långban, Sweden, by Breithaupt (1830). It also occurs at the Harstig Mine, Pajsberg, Sweden (Igelström, 1865; Sjögren, 1892) and was moderately abundant at the Franklin Mine, Franklin, Sussex County, New Jersey, from which it was described by Foshag and Gage (1925), Palache and Berman (1927), and Palache (1935). Foshag and Gage proposed that hedyphane be defined as material with Ca > Pb, leading to the formula $(Ca,Pb)_5(AsO_4, PO_4)_3Cl$, which is the one given in most modern mineralogical compendia. However, our electron microprobe survey of a large number of specimens from Franklin and Långban, some analyses of which are presented herein, has failed to produce any lead-bearing specimens which conform to the criterion of Foshag and Gage. This calls into question the chemical analysis published by these authors, who, in fact, noted that some of their material appeared to be slightly altered. Unfortunately, we were unable to locate the specimen they studied and thus it could not be reanalyzed.

The Ca > Pb criterion of Foshag and Gage creates a dilemma when one tries to formally define hedyphane. Although these authors proposed that hedyphane be considered the name for material with Ca > Pb, they were discussing their own material and not other, previously described hedyphanes, all of which contain substantial amounts of lead and whose Pb:Ca molar ratios approximate 3:2. We therefore propose that the name *hedyphane* be restricted to material which meets the following requirements: that Pb and Ca be major elements having a molar ratio of ~3:2, that As exceed P, and that Cl exceed F or (OH). Defined in this way, the ideal formula of hedyphane becomes $Ca_2Pb_3(AsO_4)_3Cl$. The niche previously assigned to this mineral, namely $(Ca,Pb)_5(AsO_4)_3Cl$ with Ca > Pb, or ideally the end-member $Ca_5(AsO_4)_3Cl$, is now vacant. Material with this ideal end-member composition has been discovered, however, and is now being characterized. When this is accomplished, it will fill the niche previously assigned to hedyphane by Foshag and Gage. This nomenclatural scheme is advantageous in that it retains the name hedyphane for those compositions previously described as hedyphane in the literature, thus ensuring continuity. This redefinition of hedyphane was proposed to the IMA Commission on New Minerals and Mineral Names as part of a submission on turneaureite and has been approved by that body.

We have chosen for the neotype hedyphane the Harvard University specimen H-90417, from Långban, Sweden. Material from this specimen has been used in a determination of the crystal structure and for the determination of the chemical, unit cell, and space group data presented herein.

Occurrence

Hedyphane occurs at Långban both in massive form and as euhedral crystals. It is frequently associated with barite, barylite, rhodonite, and numerous other phases. Having studied relatively few Långban samples, we cannot make more than this simple paragenetic generalization. The neotype specimen consists of a massive, fine-grained, calcite-bearing rock, which is coated with 1 cm euhedral calcite crystals. These are, in turn, coated with hedyphane crystals, which occur as euhedral individuals and as clusters of randomly intergrown crystals. The hedyphane is followed by sparse amounts of allactite and two generations of hausmannite.

At Franklin, hedyphane occurs in a wide variety of assemblages and is the most abundant non-silicate lead mineral at this deposit, both in terms of volume and frequency of occurrence. Among the representative modes of occurrence of Franklin hedyphane are (a) As massive, yellow to colorless, greasy-lustered material associated with barylite, copper, and curved, platey, massive calcite. (b) As colorless, yellow, or gray tabular dipyramids associated with rhodonite, barite, and manganaxinite. The morphology of these euhedral crystals was described by Palache and Berman (1927) and Palache (1935). (c) As a yellow-to-brown-to-gray massive material, filling fracture seams in willemite-franklinite ore and frequently associated with rhodonite. (d) As stout, prismatic, colorless crystals, 6×6 mm in size, associated with bright green willemite, bright pink rhodonite, and copper, all in a calcite matrix. The last-named assemblage is clearly secondary and coats a pre-existing, strongly fluorescent apatite of undetermined composition.

Physical description

The neotype hedyphane occurs as light yellow, euhedral crystals approximately 1 mm in maximum dimension. They are tabular on {0001}, and the form development is similar to that figured by Palache and Berman (1927). The morphologies of the Swedish and Franklin crystals are similar. Hedyphane is translucent with a white streak and has a greasy to vitreous luster on crystal faces and fracture surfaces. The Mohs hardness is approximately 4. Cleavage is indiscernible, the fracture is even, and the mineral is moderately brittle. Density measurements made with a Berman balance gave values ranging from 5.71 to 5.85 g/cm^3, with the latter value closest to that calculated from the ideal formula, namely 5.99 g/cm^3. Optically, neotype hedyphane is uniaxial positive with a mean index of refraction between 1.95 and 1.965. The observation is in agreement with those of Palache and Berman (1927), who found Franklin hedyphane to have indices $\epsilon = 1.958$ and $\omega = 1.948$.

Although the arsenate apatites from Franklin cannot, in general, be unambiguously identified on the basis of their varied responses to ultraviolet radiation, the lead-bearing members (mimetite and hedyphane) have a very weak, light yellow fluorescence. Johnbaumite, $Ca_5(AsO_4)_3OH$, shows a strong orange fluorescence, which is characteristic of this mineral.

Chemistry and X-ray crystallography

The samples were chemically analyzed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA, measured on brass. The standards used were synthetic PbO (Pb), fluorapatite (Ca, F, P), barite (Ba), celestite (Sr), scapolite (Cl), manganite (Mn), and arsenolite (As). The data were corrected using a modified version of the MAGIC-4 program. Zn is absent in all samples studied. The resultant analyses, together with previous analyses of hedyphane, are presented in Tables 1 and 2 in order of decreasing calcium content.

The unit cell contents of neotype hedyphane (H-90417), calculated assuming a density of 5.85 g/cm^3, are $Ca_{4.1}Pb_{5.8}Sr_{0.2}As_{5.5}P_{0.1}O_{23.2}Cl_{2.1}$ or, ideally, $Ca_2Pb_3(AsO_4)_3Cl$ with Z = 2. X-ray powder diffraction data were obtained from the same sample utilizing a 114.6 mm diameter Gandolfi camera, a polycrystalline sample, Cu$K\alpha$ radiation, and NBS silicon ($a = 5.43088$Å) as an internal standard. The data are given in Table 3.

Fragments of a euhedral crystal from the same specimen were studied by the precession method using Mo$K\alpha$ radiation. The space group of hedyphane is $P6_3/m$, the crystal structure having been refined successfully in this symmetry. No monoclinic superstructure reflections were evident on overexposed precession photographs taken with unfiltered radiation. The unit cell parameters, refined by least-squares from the powder data in Table 1, are $a = 10.140(3)$ and $c = 7.185(4)$Å. These values are in good agreement with those calculated from weighted averages of the cell parameters of synthetic $Ca_5(AsO_4)_3Cl$

Table 1. Electron microprobe analyses of hedyphane and related species from Franklin, New Jersey

Specimen	CaO	SrO	BaO	PbO	P₂O₅	As₂O₅	Cl	O=Cl,F	Total
C6270-1	45.4			1.4	8.5	42.5	2.1	0.8	100.7[a]
C6270-2	45.1			1.5	7.9	42.6	2.2	0.8	99.9[a]
Foshag(1925)	14.98			52.77		29.94	2.98	0.67	100.86[b]
C6277-1	11.1	0.8	0.4	56.0	0.4	28.8	3.3	0.7	100.6[c]
C4145	10.6	3.5	0.4	51.2	0.3	30.1	3.3	0.7	99.1
H90003	10.0	3.4	0.3	54.2	0.3	28.7	3.4	0.8	99.5
R5301-3	9.8	6.6	0.9	50.0	0.3	30.2	3.5	0.8	100.5
Hedyphane	9.72			58.02		29.88	3.07	0.69	100.00[d]
C6276	9.5	4.4	1.1	52.2	0.3	29.1	3.3	0.7	99.2
H107890	9.1	7.0	0.5	52.0	0.2	29.1	3.4	0.8	100.5
H97913	9.0	6.9	0.6	52.0	0.2	29.5	3.4	0.8	100.8
R5301-1	8.9	6.1	0.8	51.2	0.2	29.2	3.3	0.7	99.0
R6552	8.2	0.9	0.6	59.3	0.6	27.2	3.1	0.7	99.2
H90006	7.9	8.4	0.4	52.5	0.2	29.9	3.3	0.7	101.9
H105459	7.1	1.2	0.3	63.4	0.8	26.4	3.1	0.7	101.6
H105462	5.9	1.4	1.1	62.2	1.3	24.0	3.0	0.7	98.2[e]
Mimetite				74.99		23.17	2.38	0.54	100.00[e]

[a]Includes 0.6% MnO, 0.8% F, traces of BaO, and 0.2% H₂O (in C6270-1).

[b]Includes 0.28% (FeO + MnO), 0.10% MgO, 0.23% ZnO, 0.08% H₂O, and 0.17% insoluble residue.

[c]Includes 0.5% MnO.

[d]Theoretical composition of hedyphane, Ca₂Pb₃(AsO₄)₃Cl.

[e]Theoretical composition of mimetite, Pb₅(AsO₄)₃Cl.

Accuracy of microprobe data is ± 4% of amount present. Fluorine is absent or present in traces except as noted.

Table 2. Electron microprobe analyses of hedyphane and related species from Långban, Sweden

Specimen	CaO	BaO	PbO	P₂O₅	As₂O₅	Cl	O=Cl,F	Total
134981	43.8		0.7	6.1	44.9	3.2	1.2	100.6[a]
B13171	42.9		1.2	2.2	50.1	2.4	1.1	100.7[a]
H105545	12.0	0.1	57.8	0.4	29.0	3.4	0.8	101.9
Michaelson	10.50		57.45	3.19	28.51	3.06	0.69	102.02[b]
H90417	10.3	0.1	58.0	0.4	28.2	3.3	0.7	100.6
R5302-3	10.2	4.7	54.0	0.2	28.5	3.3	0.7	100.2
48983	10.0	14.1	46.0	0.5	25.3	3.4	0.7	98.5
Hedyphane	9.72		58.02		29.88	3.07	0.69	100.00[c]
R10663	9.6	4.9	55.1	1.0	27.4	2.8	0.6	100.2
H88066	9.6	3.5	56.3	0.3	28.4	3.3	0.7	100.7
C4148	9.1	5.0	57.3		27.9	3.2	0.7	101.8
PA14301	8.8	11.2	49.3	0.9	27.5	2.8	0.6	99.9
Lindström(1879)	7.85	8.27	50.89	0.55	29.01	3.14	0.71	99.57[d]
H116373	7.6	11.4	52.5	1.3	26.5	3.2	0.7	101.8
H101553	6.9	0.3	63.6	0.2	25.3	3.1	0.7	98.7
PA13951	6.0	0.4	66.3	0.2	24.8	3.0	0.7	100.0
H116366	5.4	1.0	65.3	1.0	24.5	2.9	0.7	99.4
Mimetite			74.99		23.17	2.38	0.54	100.0[e]

[a]Includes 1.9% MnO and 1.2% F in 134981 and 1.7% MnO and 1.3% F in B13171.

[b]Includes 1.0% SrO. This component was not found in other specimens.

[c]Theoretical composition of hedyphane, Ca₂Pb₃(AsO₄)₃Cl.

[d]Includes 0.25% MgO, 0.08% Fe₂O₃, 0.15% Na₂O, and 0.09% K₂O.

[e]Theoretical composition of mimetite, Pb₅(AsO₄)₃Cl.

Accuracy of microprobe data is ± 4% of the amount present. Fluorine is absent or present in traces except as noted.

and $Pb_5(AsO_4)_3Cl$ (Kreidler and Hummel, 1970), namely $a = 10.16$ and $c = 7.20$Å.

Structure refinement

A crystal fragment approximately 0.12 × 0.12 × 0.22 mm in size from specimen H-90417 was chosen for structure analysis. The intensities of 550 reflections having sin$\theta \leq 0.460$ were measured with a Supper-Pace diffractometer system using Weissenberg equi-inclination geometry, monochromatized Mo$K\alpha$ radiation, and a scanning rate of 2°/min. Intensities of four standard reflections were periodically monitored throughout the data-gathering process to check crystal and electronic stability. The data were converted to structure factor amplitudes by correction for Lorentz, polarization, and absorption effects ($\mu_l = 475$ cm^{-1}). A total of 57 reflections were unobserved and assigned intensities of $I_{min}/3$, where I_{min} is the minimum observable intensity. Structure factor calculations were carried out with the program RFINE 2 (Finger, 1972) using neutral atom scattering factors (Doyle and Turner, 1968), anomalous dispersion corrections for Pb and As (Cromer and Liberman, 1970), and the atomic coordinates in mimetite (Hendricks et al., 1932) as initial values for the positional parameters. Ca and Pb were assumed to be fully ordered in 4f and 6h, respectively, as implied by the composition. Unobserved reflections were assigned zero weight during the refinement.

Using isotropic temperature factors, the refinement converged to an unweighted conventional residual of

Table 3. X-ray powder diffraction data for hedyphane

I	d_{obsd}	d_{calc}	hkl	I	d_{obsd}	d_{calc}	hkl
4	8.77	8.78	100	<1	1.704	1.708	313
<1	5.55	5.56	101			1.706	501
4	5.070	5.070	110	<<1	1.687	1.691	412
<1	4.393	4.391	200			1.690	330
5	4.135	4.142	111	<1	1.658	1.659	420
1	3.742	3.746	201	2	1.641	1.645	331
7	3.586	3.593	002	<<1	1.614	1.618	403
4	3.316	3.325	102			1.617	421
		3.319	210	2	1.575	1.578	502
10	3.014	3.013	211			1.577	510
8	2.929	2.931	112	3	1.538	1.542	323
		2.927	300			1.541	511
<<1	2.712	2.711	301	2	1.526	1.531	304
<<1	2.540	2.535	220			1.529	332
4	2.440	2.438	212	1	1.504	1.506	422
		2.435	310	<<1	1.462	1.464	600
<<1	2.395	2.391	221	1	1.444	1.446	314
1	2.309	2.307	311			1.444	512
<<1	2.265	2.269	302			1.444	430
2	2.199	2.195	400	<1	1.432	1.434	601
2	2.166	2.166	113	1	1.390	1.390	404
<<1	2.099	2.099	401	2	1.380	1.381	333
2	2.072	2.071	222			1.380	521
2	2.016	2.016	312	<<1	1.352		
		2.015	320	1	1.339		
8	1.943	1.942	213	3	1.318		
		1.940	321	<1	1.311		
1	1.911	1.916	410	<1	1.268		
3	1.875	1.873	402	1	1.255		
1	1.853	1.854	303	<<1	1.249		
		1.852	411	<1b	1.215		
2	1.796	1.796	004	<<1	1.196		
1	1.756	1.757	322	1	1.185		
		1.756	500				

114.6 mm Debye-Scherrer camera, CuKα radiation, visually estimated intensities, b = broadened line. Indexed with the aid of the single-crystal intensities.

0.088 for all reflections. At this point possible solid solution between Ca and Pb was investigated by refining site occupancy factors. The results, 0.988(6) Ca + 0.012 Pb on the $4f$ site and 0.992(5) Pb + 0.008 Ca on the $6h$ site, indicated no statistically significant deviation from complete ordering. On the other hand, refining atomic param-

eters with these occupancy factors caused the temperature factor of Ca, which had refined to a value of 0.01Å^2 in the completely ordered model, to increase to a somewhat more reasonable value of 0.28Å^2. For this reason, ca. 1% solid solution between Ca and Pb was assumed in subsequent calculations. An analogous sensitivity of the temperature factor of La to trace amounts (1.4%) of Ca in solid solution was observed by Schroeder and Mathew (1978) in the oxyapatite $Ca_2La_8(SiO_4)_6O_2$.

When a change from isotropic to anisotropic temperature factors was made, the refinement converged to residuals of 0.076 (unweighted) and 0.062 (weighted) for all reflections. The final values of the atomic parameters and selected interatomic distances and angles are given in Tables 4 and 5, respectively. Observed and calculated structure factor amplitudes are listed in Table 6.[2]

Structure description and discussion

Atomic ordering

The most salient feature of the structure is the complete, or nearly complete, ordering of calcium and lead. This places hedyphane among the small group of natural apatites and structurally related minerals in which cation ordering is known from experiment or suspected from stoichiometry. Among these are nasonite, Pb_6Ca_4 $(Si_2O_7)_3Cl_2$ (Giuseppetti et al., 1971); ganomalite, $Pb_9Ca_5MnSi_9O_{33}$ (Dunn, Peacor, and Randall, unpublished data); caracolite, $Na_6Pb_4(SO_4)_6Cl_2$ (Schneider, 1967, 1969); and cesanite, $Ca_4Na_6(SO_4)_6(OH)_2$ (Tazzoli, 1983). Despite having the same 3:2 cation ratio, not all of these minerals have the same simple ordering scheme as

[2] To receive a copy of Table 6, order Document AM-84-247 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D. C. 20009. Please remit $5.00 in advance for the microfiche.

Table 4. Atomic coordinates and anisotropic temperature factors ($\times 10^4$) in hedyphane

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
Ca	1/3	2/3	0.009(1)	7(7)	7(7)	19(18)	3(3)	0	0	0.3(2)
Pb	0.2581(2)	0.0142(2)	1/4	18(2)	27(2)	69(3)	10(2)	0	0	0.97(4)
As	0.4021(4)	0.3895(4)	1/4	8(5)	8(5)	40(8)	1(5)	0	0	0.48(7)
O(1)	0.364(3)	0.523(3)	1/4	−10(5)	11(36)	72(66)	1(30)	0	0	0.2(5)
O(2)	0.616(3)	0.474(3)	1/4	37(40)	55(45)	15(62)	32(37)	0	0	0.3(5)
O(3)	0.365(3)	0.276(2)	0.065(3)	119(40)	51(32)	163(62)	73(31)	−133(39)	−79(35)	1.7(5)
Cl	0	0	0	58(16)	58(16)	30(37)	29(8)	0	0	1.2(3)

Estimated standard deviations are in parentheses. The anisotropic temperature factors (β) are of the form $\exp\{-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\}$. Isotropic temperature factors (B) are from the final cycle of the isotropic refinement.

Table 5. Selected interatomic distances (Å) and angles (°) in hedyphane

CaO$_9$ polyhedron

Ca-O(1)	2.38(2)	(3X)
O(2)	2.55(2)	(3X)
O(3)	2.86(2)	(3X)
mean	2.60	

PbO$_5$Cl$_2$ polyhedron

Pb-O(2)	2.36(3)		O(2)-Pb-O(3)	85.8(6)	(2X)
O(3)	2.54(2)	(2X)	O(3)-Pb-O(3)	126.2(1.1)	
O(3)	2.67(2)	(2X)	mean	99.3	
Pb-O(1)	3.45(2)	(2X)			
Cl	3.117(2)	(2X)			

AsO$_4$ tetrahedron

As-O(3)	1.66(2)	(2X)	O(3)-As-O(2)	104(1)	(2X)
O(1)	1.70(2)		O(3)-As-O(3)	106(2)	
O(2)	1.73(3)		O(1)-As-O(2)	111(1)	
mean	1.69		O(3)-As-O(1)	115(1)	(2X)
			mean	109	

O(3)-O(3)	2.66(5)	
O(2)-O(3)	2.68(3)	(2X)
O(1)-O(3)	2.83(3)	(2X)
O(1)-O(2)	2.83(4)	

Shortest distances

Ca-Ca	3.46(2)	As-As	4.114(4)
Pb-Pb	4.404(2)	Cl-Cl	3.593(2)
Pb-Ca	4.208(5)	O(3)-Cl	3.38(2)
Ca-As	3.387(6)	O(3)-O(3)	2.66(5)
Pb-As	3.305(4)		

Estimated standard deviations are in parentheses. Two and three identical distances are denoted by 2X and 3X, respectively.

hedyphane. The hexagonal polymorph of caracolite, for example, has 4 Na in $4f$ and (4Pb + 2Na) in $6h$ (Schneider, 1967).

Of the synthetic apatites with a 3:2 cation ratio, ordering has been confirmed experimentally in only a few. One such case is $Ca_4Pb_6(PO_4)_6(OH)_2$, which Engel et al. (1975) found to be fully ordered with Ca in $4f$ and Pb in $6h$ as in hedyphane. By contrast, Cockbain and Smith (1967) found $Ca_4La_6(SiO_4)_6(OH)_2$ to be disordered. Unfortunately, both of these determinations are subject to some doubt, as they were derived from analysis of a very small number of powder X-ray reflections. A full crystal structure analysis of an apatite of the 2:8 type, $Ca_2La_8(SiO_4)_6O_2$, was performed by Schroeder and Mathew (1978), who found (2Ca + 2La) in $4f$ and 6 La in $6h$. This is the inverse of the ordering in caracolite in the sense that the 4-fold rather than the 6-fold site has mixed occupancy.

Although cation ordering has been demonstrated in hedyphane, there is no evidence for displacement of the chlorine atoms from their ideal positions at 0,0,0 and 0,0,½ as is the case in monoclinic chlorapatite (Mackie et al., 1972). The temperature factors of the Cl atom are not

unreasonably large and its rms thermal displacement along the **c** axis is only 0.090Å, indicating no displacement from the ideal positions. This accounts for the maintenance of hexagonal symmetry in hedyphane, since chlorine displacements would produce a monoclinic superstructure with a doubling of one of the **a** cell dimensions as in chlorapatite.

In addition to ordering phenomena, some comment is necessary concerning the changes in the position of the O(1) atom in hedyphane, vanadinite ($Pb_5(VO_4)_3Cl$), and finnemanite ($Pb_5(AsO_3)_3Cl$) and the consequences for cation coordination in these chlorapatite isotypes. Comparisons with mimetite ($Pb_5(AsO_4)_3Cl$) and pyromorphite ($Pb_5(PO_4)_3Cl$) would also be useful here, but well-refined structures are not available for these minerals. In vanadinite (Trotter and Barnes, 1958) the longest Pb–O bond is between Pb(2) (which corresponds to the Pb site in hedyphane) and O(1) at 3.17(4)Å. A second Pb(2)–O(1) distance of 3.80(4)Å is too long to represent a chemical bond. In hedyphane the Pb–O(1) distance is further lengthened to 3.45(2)Å (two equal distances), which represents a very weak interaction at best. The Pb atom in hedyphane is therefore essentially in 7-fold coordination (Fig. 1), rather than the 8-fold coordination usual in chlorapatite isotypes. The limiting case occurs in finnemanite (Effenberger and Pertlik, 1979), in which O(1) is altogether absent from the structure, leaving Pb(2) in an unambiguous 7-fold coordination, AsO_3 trigonal pyramids rather than AsO_4 tetrahedra, and $Pb(1)_2O_9$ groups, which strongly resemble Pb–Pb metal clusters.

If the two O(1) atoms in Figure 1 are not bonded to Pb, it is obvious that the lead atom has a decidedly asymmetrical, "one-sided" coordination. It is also perhaps significant that the shortest and presumably strongest Pb–O bond, that to O(2) at 2.36(2)Å, is apposed to the two distant, nonbonded O(1) atoms. This one-sided coordination of Pb(II) is very common and is usually attributed to repulsions between a sterically active $6s^2$ electron lone pair on the lead atom and the neighboring anions (Galy et al., 1975). In the structures of hedyphane and vanadinite (and probably the other lead chloride apatites as well), the lone pair is presumably directed towards the two distant O(1) atoms. On the other hand, in vanadinite the lone pair effect is not manifest in the environment of the Pb(1) atom (which corresponds to the Ca site in hedyphane). The Pb(1)–O distances are 2.47, 2.57, and 2.76Å, which are less than or equal to the sum of the ionic radii for 9-coordinated Pb^{2+} (Shannon, 1976), and the coordination polyhedron (a distorted tricapped trigonal prism) is very like that around the analogous Ca(1) site in chlorapatite, a mineral which contains no lone pair ions.

If the structure of hexagonal chlorapatite (Brosnahan, 1977) is regarded as the prototype for those of hedyphane and its congeners, a comparison of the Ca(1) and Ca(2) coordination polyhedra in chlorapatite suggests a reason why hedyphane and $Ca_4Pb_6(PO_4)_6(OH)_2$ have ordered
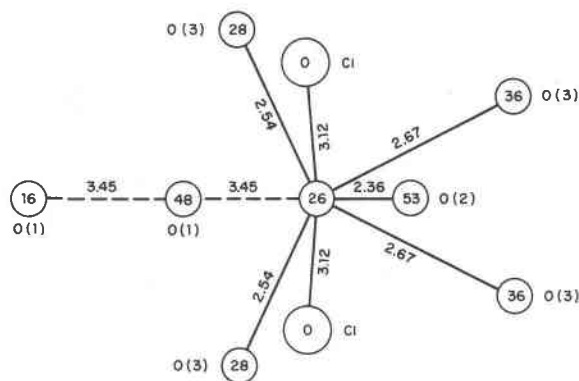
Fig. 1. Projection on (100) of the coordination polyhedron around the Pb site in hedyphane. Numerals within the circles are the x coordinates of the atoms.
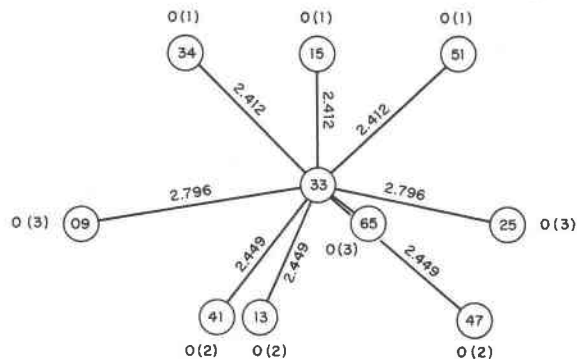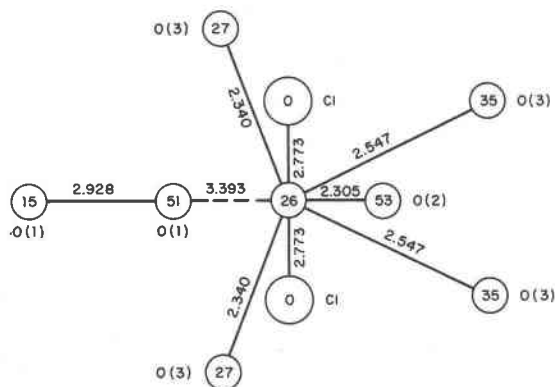

Fig. 3. Projection on (100) of the coordination polyhedron around the Ca(1) site in chlorapatite. Numerals within the circles are the x coordinates of the atoms.

cations, while $Ca_4La_6(SiO_4)_6(OH)_2$ does not. Inspection of Figure 2 shows that the polyhedron around the Ca(2) or $6h$ site in chlorapatite has an irregular, nearly one-sided configuration, which can be made even more so by further withdrawing the O(1) ligand. The Ca(2)–O(1) distance of 2.928(1)Å is the longest Ca-ligand separation in the structure and must surely represent a very weak bond. By contrast, the nine ligands around the Ca(1) or $4f$ site shown in Figure 3 completely surround the central cation with a polyhedron which is less amenable to the kind of distortion produced by sterically active lone pairs. The $6h$ site is therefore "ready made" for such ions, which prefer a highly asymmetrical, one-sided environment to accommodate the lone pair. On the other hand, ions with noble gas configurations, e.g., Ca^{2+}, should either exhibit a preference for the more symmetrically coordinated $4f$ site or, more probably, no preference at all. We suggest that this is the reason, or at least one of the reasons, for cation ordering in hedyphane. In $Ca_4La_6(SiO_4)_6(OH)_2$ both cations have noble gas configurations,

hence there is no strong site preference, and Ca^{2+} and La^{3+} are disordered over both positions.

Solid solutions

The majority of the samples studied were hedyphane, which is essentially fully ordered with calcium in the $4f$ site and lead in the $6h$ site. Such ordering has several consequences, the most important being that it implies the possibility of a solvus in the system $Ca_5(AsO_4)_3Cl$–$Pb_5(AsO_4)_3Cl$. For this reason we have conducted a survey of phases from Franklin and Långban (Tables 1 and 2), whose compositions lie approximately in this system. Correlation of these and other, still unpublished analyses shows that while compositions from mimetite ($Pb_5(AsO_4)_3Cl$) to hedyphane ($Ca_2Pb_3(AsO_4)_3Cl$) are well-represented, there is none between hedyphane and the as-yet-undescribed end-member $Ca_5(AsO_4)_3Cl$. Specifically, the apparent gap extends from $Ca_{4.8}Pb_{0.2}$ to $Ca_{2.3}Pb_{2.7}$, grouping Sr and Ba with Pb. This finding is compatible with, but does not prove, the existence of a solvus in this system. Should phases with compositions between the above limits be found, they should be examined for exsolution lamellae or other fine-scale domains differing in composition by the limits of the apparent solvus.

Ordering of lead and calcium was also observed by Engel et al. (1975) in the synthetic system $Ca_5(PO_4)_3OH$–$Pb_5(PO_4)_3OH$. They noted, among other things, the existence of the ordered compound $Ca_4Pb_6(PO_4)_6(OH)_2$, which is the phosphate hydroxide analogue of hedyphane, and complete solid solution between lead and calcium. The latter observation may have been due to the high temperatures and very short times used for their syntheses, however. On the other hand, Verbeeck et al. (1981), working in the same system, found an apparent solvus between the compositions $Ca_9Pb(PO_4)_6(OH)_2$ and $Ca_6Pb_4(PO_4)_6(OH)_2$, which approximately coincides with the limits we have observed in the natural arsenate analogues.

The ordering of cations in hedyphane may have impor-

Fig. 2. Projection on (100) of the coordination polyhedron around the Ca(2) site in chlorapatite. Numerals within the circles are the x coordinates of the atoms.

tant implications for solid solutions in other apatites. Few structures exhibit such a wide range of ionic substitutions as does the apatite structure (nearly half the elements in the periodic table according to Roy et al. (1978)). In particular, it may be predicted from the apparent special compatibility of the 6h site with large cations having nonbonded valence electron pairs that such atoms will always exhibit a preference for this site. At least a partial ordering of Pb(II), Sn(II), Bi(III), Sb(III), Tl(I), Ge(II), and Te(IV), where they occur in the apatite structure, may be expected. This may, in turn, affect physical and chemical properties. One example is the property of luminescence, if the structure contains activator ions in addition to the lone pair atoms listed above. In fact, Sb(III) is itself an activator in apatites and has been proposed to preferentially occupy the 6h site, albeit for reasons other than the one given here (Blasse, 1975). A second example is the degree of uptake of toxic elements into the apatite of human bones and teeth. All of the aforementioned elements exhibit heavy metal toxicity in humans in varying degrees.

Insofar as the minor elements in hedyphane are concerned, Tables 1 and 2 show that Sr is the chief cationic substituent in Franklin hedyphanes, whereas at Långban, this role is filled by Ba. The maximum SrO content observed in hedyphane is 8.4 wt.%, equivalent to 0.88 Sr per 5 total cations. The maximum BaO content is 22 wt.%, equivalent to 1.5 Ba per 5 total cations, this being in an unpublished analysis. Both Ba and Sr substitute for Pb, as shown by sympathetic variations among these elements. This is consistent with their ionic radii, which favor their substitution for Pb rather than Ca. No samples were found with Ba > Pb; such material would be classified as morelandite, $(Ba,Pb,Ca)_5(AsO_4)_3Cl$, a mineral currently known only from Jakobsberg, Sweden (Dunn and Rouse, 1978).

Based on the previous definition of these arsenate apatites, i.e., $(Ca,Pb)_5(AsO_4)_3Cl$ compositions with Ca > Pb being hedyphane and those with Pb > Ca being mimetite, Dunn et al. (1980) reported that most of the material from Franklin and Långban was calcian mimetite. That statement must now be revised in light of the recognition of hedyphane as an ordered species intermediate between the unnamed species $Ca_5(AsO_4)_3Cl$ and $Pb_5(AsO_4)_3Cl$ (mimetite). Most of the specimens described by Dunn et al. are now shown to be hedyphane. It should be noted, however, that true mimetite does, in fact, occur at both Franklin and Långban.

Acknowledgments

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