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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 4*f* and 6*h*, 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 6*h* 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 $2.3 \leq x \leq 4.8$, 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 nonequivalent cation sites. The A site corresponds to equipoint 4*f* and is coordinated by nine oxygen atoms at the vertices of a distorted tricapped trigonal prism, whereas the B site corresponds to equipoint 6*h* 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.

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Table 6. Observed and calculated structure factors for hedyphane

H	K	L	F(OBS)	F(CALC)	H	K	L	F(OBS)	F(CALC)
2	1	0	150.1	162.6	1	8	0	65.7	70.4
3	1	0	107.7	114.2	2	8	0	31.0	31.9
4	1	0	236.8	222.6	3	8	0	89.6	94.3
5	1	0	190.2	153.0	4	8	0	98.9	99.7
6	1	0	140.1	96.9	5	8	0	13.2 *	10.4
7	1	0	218.2	192.7	0	9	0	38.8	37.0
1	2	0	128.2	113.5	1	9	0	33.1	33.6
2	2	0	67.7	73.3	2	9	0	31.1	23.9
3	2	0	58.6	64.0	3	9	0	207.6	231.0
4	2	0	132.5	136.4	0	10	0	70.4	70.7
5	2	0	61.8	61.6	1	10	0	30.3	31.8
6	2	0	75.7	69.6	2	10	0	59.5	66.1
7	2	0	14.7 *	4.5	0	11	0	11.7 *	12.2
0	3	0	278.6	288.1	2	0	1	122.0	83.4
1	3	0	91.1	80.3	3	0	1	89.6	60.5
2	3	0	186.8	191.7	4	0	1	81.7	61.8
3	3	0	78.6	80.0	5	0	1	68.9	60.8
4	3	0	42.0	27.6	6	0	1	179.4	170.9
5	3	0	22.0	33.3	7	0	1	51.3	51.2
6	3	0	125.0	120.6	1	1	1	144.6	144.3
7	3	0	123.3	103.9	2	1	1	321.6	345.9
0	4	0	271.3	283.0	3	1	1	49.2	48.3
1	4	0	129.5	119.4	4	1	1	61.1	61.0
2	4	0	172.5	167.0	5	1	1	282.8	223.9
3	4	0	203.6	211.0	6	1	1	125.3	96.3
4	4	0	259.7	276.3	7	1	1	111.6	94.3
5	4	0	57.2	52.4	0	2	1	88.0	83.4
6	4	0	43.3	42.6	1	2	1	306.9	322.1
7	4	0	95.1	84.3	2	2	1	47.5	39.7
0	5	0	168.1	169.8	3	2	1	175.7	184.6
1	5	0	107.7	105.7	4	2	1	102.6	103.0
2	5	0	40.0	40.8	5	2	1	237.6	231.3
3	5	0	201.6	213.3	6	2	1	13.8 *	13.1
4	5	0	59.4	59.4	7	2	1	147.4	116.5
5	5	0	20.8	13.6	0	3	1	67.3	60.5
6	5	0	31.9	26.3	1	3	1	144.2	137.8
7	5	0	134.0	126.8	2	3	1	256.1	275.7
0	6	0	98.5	96.3	3	3	1	228.2	238.8
1	6	0	154.1	153.2	4	3	1	10.8 *	9.6
2	6	0	85.1	88.1	5	3	1	47.9	49.5
3	6	0	10.3 *	25.8	6	3	1	275.9	272.0
4	6	0	90.9	109.8	7	3	1	94.6	76.0
5	6	0	131.4	148.4	0	4	1	62.6	61.8
6	6	0	43.7	45.8	1	4	1	43.1	42.4
7	6	0	14.8 *	33.6	2	4	1	34.7	33.6
0	7	0	110.4	104.0	3	4	1	29.6	28.1
1	7	0	107.4	103.1	4	4	1	71.7	74.7
2	7	0	145.8	150.5	5	4	1	26.1	32.5
3	7	0	29.2	34.3	6	4	1	94.3	89.6
4	7	0	44.6	53.3	7	4	1	14.1 *	2.8
5	7	0	12.3 *	1.6	0	5	1	66.6	60.8
6	7	0	36.4	43.7	1	5	1	170.0	170.8
0	8	0	233.1	232.6	2	5	1	91.4	88.6

H	K	L	F(OBS)		F(CALC)
3	5	1	10.2	*	15.6
4	5	1	47.3		49.5
5	5	1	134.2		137.7
6	5	1	29.9		24.0
7	5	1	37.2		32.8
0	6	1	172.8		170.9
1	6	1	153.1		147.7
2	6	1	37.0		31.0
3	6	1	98.4		105.0
4	6	1	103.2		109.0
5	6	1	207.2		224.2
6	6	1	36.6		33.5
7	6	1	14.3	*	6.6
0	7	1	61.6		51.2
1	7	1	33.2		30.6
2	7	1	195.5		204.5
3	7	1	93.8		98.2
4	7	1	48.8		55.8
5	7	1	32.9		17.4
6	7	1	143.5		156.8
0	8	1	27.2		30.2
1	8	1	94.2		95.7
2	8	1	83.4		78.8
3	8	1	11.0	*	12.6
4	8	1	59.1		64.7
0	9	1	108.5		101.6
1	9	1	115.6		127.2
2	9	1	116.0		122.4
3	9	1	11.9	*	2.8
0	10	1	86.4		89.3
1	10	1	95.0		103.0
2	10	1	90.1		94.9
0	11	1	112.6		114.1
2	0	2	37.4		19.0
3	0	2	84.8		72.4
4	0	2	337.8		299.9
5	0	2	218.1		204.0
6	0	2	194.1		175.4
7	0	2	118.9		119.0
1	1	2	248.6		255.5
2	1	2	97.4		101.6
3	1	2	163.2		160.2
4	1	2	68.7		55.6
5	1	2	164.1		143.0
6	1	2	78.0		64.7
7	1	2	82.2		65.1
0	2	2	27.3		19.0
1	2	2	173.4		167.1
2	2	2	205.1		209.0
3	2	2	75.6		76.1
4	2	2	170.5		169.0
5	2	2	61.9		53.5
6	2	2	35.8		35.3
7	2	2	32.7		11.5
0	3	2	77.8		72.4
1	3	2	46.5		33.2
2	3	2	135.2		129.4
3	3	2	176.2		175.6
4	3	2	11.1	*	4.2
5	3	2	12.3	*	12.2
6	3	2	205.4		191.2
7	3	2	89.6		74.7
0	4	2	293.8		299.9
1	4	2	27.9		9.7
2	4	2	153.5		151.7
3	4	2	229.6		230.1
4	4	2	177.2		167.4
5	4	2	40.9		29.9
6	4	2	30.2		28.7
7	4	2	14.0	*	18.2
0	5	2	205.2		204.0
1	5	2	117.4		112.1
2	5	2	114.7		109.5
3	5	2	217.7		231.9
4	5	2	62.4		68.3
5	5	2	92.2		93.6
6	5	2	12.7	*	5.5
7	5	2	153.7		147.9
0	6	2	178.9		175.4
1	6	2	148.2		139.5
2	6	2	73.6		69.2
3	6	2	94.8		100.1
4	6	2	74.1		76.3
5	6	2	123.3		126.2
6	6	2	36.9		37.6
0	7	2	129.8		119.0
1	7	2	24.7		25.8
2	7	2	131.3		139.3
3	7	2	27.0		31.2
4	7	2	11.7	*	12.6
5	7	2	31.2		8.0
0	8	2	242.1		227.2
1	8	2	42.3		39.5
2	8	2	114.0		124.0
3	8	2	94.6		96.9
4	8	2	106.1		120.6
0	9	2	38.5		37.8
1	9	2	10.8	*	13.7
2	9	2	23.0		4.1
3	9	2	146.1		151.8
0	10	2	55.5		61.8
1	10	2	74.5		94.0
0	11	2	11.6	*	8.8
2	0	3	10.7	*	20.2
3	0	3	57.1		58.7
4	0	3	42.9		44.6

H	K	L	F(OBS)	F(CALC)	H	K	L	F(OBS)	F(CALC)
5	0	3	22.6	13.9	4	7	3	47.1	44.3
6	0	3	169.4	172.4	5	7	3	12.9 *	27.1
7	0	3	66.8	65.2	0	8	3	18.4	18.0
1	1	3	168.2	170.6	1	8	3	85.1	85.1
2	1	3	256.0	284.6	2	8	3	75.2	73.8
3	1	3	90.9	81.7	3	8	3	11.5 *	10.1
4	1	3	65.1	52.6	4	8	3	37.0	42.6
5	1	3	203.8	184.9	0	9	3	113.3	104.4
6	1	3	88.2	78.3	1	9	3	115.8	119.6
7	1	3	83.8	81.3	2	9	3	94.4	107.5
0	2	3	21.4	20.2	0	10	3	92.1	96.1
1	2	3	287.5	287.9	1	10	3	94.9	92.7
2	2	3	18.3	19.2	2	0	4	32.5	28.5
3	2	3	176.8	175.5	3	0	4	192.2	191.7
4	2	3	104.4	98.7	4	0	4	207.2	225.0
5	2	3	240.3	219.3	5	0	4	139.3	152.6
6	2	3	29.7	24.1	6	0	4	62.0	67.0
7	2	3	99.2	102.7	7	0	4	91.1	93.5
0	3	3	62.4	58.7	1	1	4	84.7	84.3
1	3	3	133.7	129.1	2	1	4	110.8	105.3
2	3	3	192.9	194.8	3	1	4	115.5	107.9
3	3	3	197.0	196.1	4	1	4	176.8	162.2
4	3	3	40.9	33.5	5	1	4	121.8	128.6
5	3	3	67.5	64.1	6	1	4	69.2	67.1
6	3	3	263.3	242.9	7	1	4	147.9	147.2
7	3	3	100.1	92.1	0	2	4	35.3	28.5
0	4	3	41.5	44.6	1	2	4	122.5	113.1
1	4	3	54.5	51.3	2	2	4	51.5	54.3
2	4	3	44.0	41.9	3	2	4	58.2	56.3
3	4	3	32.6	35.0	4	2	4	147.6	136.7
4	4	3	47.1	46.9	5	2	4	49.0	41.2
5	4	3	48.5	36.0	6	2	4	49.3	45.8
6	4	3	73.4	73.7	7	2	4	10.9 *	4.6
7	4	3	13.0 *	2.5	0	3	4	202.6	191.7
0	5	3	20.9	13.9	1	3	4	26.6	15.2
1	5	3	159.7	151.0	2	3	4	135.9	128.5
2	5	3	82.6	79.5	3	3	4	58.0	54.6
3	5	3	10.5 *	12.5	4	3	4	34.5	20.0
4	5	3	45.4	34.9	5	3	4	12.6 *	20.1
5	5	3	121.0	122.9	6	3	4	99.0	91.0
6	5	3	25.3	29.2	7	3	4	76.2	77.8
7	5	3	28.4	18.7	0	4	4	230.0	225.0
0	6	3	172.4	172.4	1	4	4	115.7	104.4
1	6	3	126.5	120.6	2	4	4	136.8	128.9
2	6	3	39.4	37.6	3	4	4	173.2	177.4
3	6	3	75.5	74.8	4	4	4	243.9	231.4
4	6	3	86.5	86.0	5	4	4	39.7	28.2
5	6	3	197.2	198.8	6	4	4	38.0	39.5
6	6	3	40.4	26.2	7	4	4	86.3	76.2
0	7	3	67.9	65.2	0	5	4	163.2	152.6
1	7	3	53.0	49.9	1	5	4	101.4	92.6
2	7	3	181.7	195.4	2	5	4	10.1 *	10.9
3	7	3	80.5	78.9	3	5	4	180.8	180.5

H	K	L	F(OBS)		F(CALC)	H	K	L	F(OBS)		F(CALC)
4	5	4	49.3		46.6	2	4	5	41.4		35.3
5	5	4	37.5		15.3	3	4	5	10.7	*	22.0
6	5	4	29.8		20.8	4	4	5	59.9		54.7
0	6	4	70.3		67.0	5	4	5	12.5	*	18.1
1	6	4	137.0		133.3	6	4	5	83.1		75.9
2	6	4	82.3		77.8	0	5	5	54.7		48.1
3	6	4	11.1	*	11.5	1	5	5	117.3		112.3
4	6	4	73.6		83.7	2	5	5	64.5		61.8
5	6	4	130.3		121.0	3	5	5	10.9	*	10.1
0	7	4	88.1		93.5	4	5	5	57.9		46.7
1	7	4	98.3		95.5	5	5	5	119.8		105.3
2	7	4	125.8		123.1	6	5	5	13.0	*	18.5
3	7	4	11.7	*	24.1	0	6	5	120.5		116.9
4	7	4	53.2		52.6	1	6	5	119.3		114.2
0	8	4	185.4		187.5	2	6	5	27.2		18.1
1	8	4	42.7		50.2	3	6	5	85.1		81.3
2	8	4	32.6		36.0	4	6	5	96.8		94.2
3	8	4	68.0		69.7	5	6	5	184.1		169.4
0	9	4	46.8		35.3	0	7	5	37.2		33.9
1	9	4	25.4		22.3	1	7	5	10.3	*	17.5
2	9	4	12.4	*	23.4	2	7	5	154.8		145.8
0	10	4	54.6		57.2	3	7	5	77.2		77.9
2	0	5	58.5		62.5	0	8	5	31.8		28.3
3	0	5	22.0		38.0	1	8	5	83.6		84.5
4	0	5	41.0		40.7	2	8	5	62.1		59.8
5	0	5	48.2		48.1	0	9	5	79.2		74.7
6	0	5	107.8		116.9	1	9	5	96.9		100.4
7	0	5	29.2		33.9	2	0	6	18.0		19.8
1	1	5	82.1		89.1	3	0	6	58.3		64.9
2	1	5	234.6		239.1	4	0	6	155.6		178.9
3	1	5	36.4		40.1	5	0	6	105.9		119.7
4	1	5	46.0		41.9	6	0	6	118.7		130.5
5	1	5	157.6		168.3	7	0	6	73.2		75.2
6	1	5	65.1		64.4	1	1	6	160.9		166.1
7	1	5	69.9		69.7	2	1	6	85.9		79.2
0	2	5	64.7		62.5	3	1	6	86.4		79.9
1	2	5	204.1		202.5	4	1	6	34.1		37.6
2	2	5	29.2		29.7	5	1	6	77.6		85.1
3	2	5	122.8		123.1	6	1	6	46.7		50.0
4	2	5	65.9		66.1	7	1	6	53.6		51.2
5	2	5	164.4		161.5	0	2	6	24.4		19.8
6	2	5	10.4	*	11.5	1	2	6	66.8		69.1
7	2	5	75.8		89.3	2	2	6	119.2		124.2
0	3	5	36.4		38.0	3	2	6	54.0		45.7
1	3	5	87.8		88.1	4	2	6	87.8		84.4
2	3	5	201.0		204.7	5	2	6	43.9		35.0
3	3	5	166.5		165.8	6	2	6	30.7		31.5
4	3	5	11.5	*	4.6	7	2	6	10.0	*	9.7
5	3	5	29.2		29.1	0	3	6	74.0		64.9
6	3	5	194.7		198.6	1	3	6	33.1		29.6
7	3	5	45.3		47.3	2	3	6	98.8		92.3
0	4	5	42.4		40.7	3	3	6	127.7		122.1
1	4	5	26.8		25.3	4	3	6	11.4	*	6.2

H	K	L	F(OBS)	F(CALC)
5	3	5	22.7	13.9
6	3	6	134.5	140.1
0	4	6	187.7	178.9
1	4	5	24.3	10.6
2	4	6	103.2	100.0
3	4	6	149.5	142.9
4	4	6	116.9	105.3
5	4	6	41.0	37.1
6	4	6	22.5	15.4
0	5	6	122.1	119.7
1	5	6	68.9	63.5
2	5	5	59.3	53.4
3	5	6	164.6	151.6
4	5	6	47.9	46.6
5	5	6	54.4	58.8
0	6	6	132.3	130.5
1	6	6	87.9	86.0
2	6	6	58.4	49.0
3	6	6	77.0	80.1
4	6	6	56.5	59.3
0	7	6	78.6	75.2
1	7	6	10.3 *	8.6
2	7	6	94.4	95.2
0	8	6	161.2	159.9
1	8	6	31.1	34.3
2	0	7	8.5 *	17.1
3	0	7	28.5	32.9
4	0	7	17.4	36.4
5	0	7	28.5	14.4
6	0	7	94.2	103.6
7	0	7	33.1	39.5
1	1	7	74.1	75.5
2	1	7	160.0	151.1
3	1	7	33.0	27.7
4	1	7	36.2	33.8
5	1	7	98.6	104.0
6	1	7	52.1	62.5
0	2	7	7.7 *	17.1
1	2	7	160.1	164.5
2	2	7	10.6 *	21.2
3	2	7	112.6	103.4
4	2	7	59.7	66.3
5	2	7	125.2	132.6
6	2	7	9.8 *	2.0
0	3	7	26.0	32.9
1	3	7	84.7	83.9
2	3	7	116.8	119.4
3	3	7	131.2	125.8
4	3	7	10.8 *	24.3
5	3	7	41.5	43.4
0	4	7	36.2	36.4
1	4	7	26.6	25.1
2	4	7	27.4	12.9
3	4	7	31.8	11.4
4	4	7	48.2	40.2
0	5	7	18.4	14.4
1	5	7	98.6	100.2
2	5	7	52.4	46.3
3	5	7	11.4 *	9.7
0	5	7	108.6	103.6
1	6	7	70.1	66.0
2	6	7	38.4	29.7
0	7	7	36.1	39.5