

Hedyphane from Nežilovo, Macedonia

Vladimir BERMANEC¹, Dražen BALEN¹, Roland OBERHÄNSLI²
and Stjepan ŠČAVNIČAR¹

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Abstract

Two different members of lead calcium arsenate series of apatite group from Nežilovo are found. According to the chemical formula (calculated on the basis of 10 cations), infra red absorption powder spectra, X-ray powder patterns and unit cell dimensions these are two distinct members of one mineral species. Unit cell dimensions are $a=10.157(3)$, $c=7.256(6)$ and $a=10.154(2)$, $c=7.191(3)$ Å. The first sample has Pb:Ca ratio 7.35:2.59 and the second one 6.54:3.45, what is closer to ideal hedyphane formula (6:4).

1. INTRODUCTION

Hedyphane, $Pb_3Ca_2(AsO_4)_3Cl$ is a rare member of the apatite group, closely related to mimetite, originally described from the type locality in Långban, Sweden. It occurs at the Pajsberg and Soegrufvan (Sweden) and it is most abundant non-silicate lead mineral in Franklin (New Jersey, USA).

At Långban hedyphane occurs both in massive form and as crystals in paragenesis with barite, barylite, rhodonite and numerous other phases (ROUSE et al., 1984).

At Franklin hedyphane occurs as anhedral grains, as tabular dypiramids, and as stout, prismatic crystals associated with barylite, copper, rhodonite, manganaxinite, willemite and other minerals (ROUSE et al., 1984).

The Nežilovo locality is situated around 40 km SW from Veles (Macedonia) in the central part of Pelagonian massif. A complex polymetamorphic series of Precambrian rocks can be roughly divided into an upper and lower part. The upper part consists of massive, mostly dolomitic marbles, which are approximately 1600 m thick, sometimes with calcitic sequences. The lower schistose part, so called "mixed series", which is approximately 500 m thick, consists of gneisses, mica schists, barite-bearing schists, quartz-cymrite schists and pink dolomitic marbles (BARIĆ &

IVANOV, 1960; STOJANOV, 1960). A zone with rare minerals is located between lower gneisses and upper marbles.

In Nežilovo area arsenates are found in dolomitic marble as massive-irregular grains and in a rock with quartz in the upper part of "mixed series". Undissolved residue of marble also contained hematite, magnetoplumbite, barite, piemontite, talc, muscovite and albite.

Hedyphane is rare mineral and is often in an unusual association. This study investigate paragenetic and other properties of this mineral species. We have also tried to explain role of Ba and some other elements present in Nežilovo in increased concentrations (e.g. As, Cu, Zn, Pb, Mn).

There is strong positive geochemical anomaly of Ba in Nežilovo area mostly due to large quantities of barite. In addition to increased concentrations of Ba, the Nežilovo area features positive geochemical anomalies of Zn, Pb, Cu, Mn, Ti and As (JANČEV, 1978; BERMANEC, 1992). During investigations of the rocks from "mixed series" several rare minerals have been determined by XRD: cymrite, ardennite, gahnite, sanbornite (in schists); magnetoplumbite, tilasite, hedyphane, piemontite, ardennite and gahnite (in marbles).

2. MATERIALS AND METHODS

Two samples were submitted to investigation; one has been found (in tectonic zone) on the contact of "mixed series" and marbles from upper part of series and the other is in quartz vein from upper part of "mixed series". In both cases lead-calcium arsenates anhedral grains are more than one centimeter in size, yellowish white, with white streak and greasy luster. The Mohs hardness is approximately 4. Cleavage is distinct and parallel to {0001}. They are not fluorescent under UV light.

The X-ray powder patterns were recorded on a Phillips vertical X-ray goniometer, using $CuK\alpha$ radiation, with graphite monochromator, and NaCl as an internal standard. Unit cell dimension were calculated with the aid of the program GITTER (HUMMEL, pers. com.).

The samples were analyzed by electron microprobe, to examined homogeneity and chemical composition. Used standards were: wollastonite (Ca), pure As, and

¹ Mineraloško-petrografski zavod PMF-a, Demetrova 1, 41000 ZAGREB, CROATIA

² Institut für Geowissenschaften Universität Mainz, Saarstr. 21, D-6500 MAINZ, DEUTSCHLAND

			SAMPLE I		SAMPLE II		Långban	
h	k	l	d_{hkl}	I_{ob}	d_{hkl}	I_{ob}	d_{hkl}	I_{ob}
1	0	0	8.74	0.3	8.79	0.5	8.77	4
1	0	1			5.560	0.1	5.55	<1
1	1	0	5.050	0.4	5.068	1.0	5.070	4
2	0	0	4.379	0.8	4.396	0.3	4.393	<1
1	1	1	4.152	2.9	4.144	2.0	4.135	5
*			4.005	0.1				
2	0	1	3.757	0.7	3.757	0.5	3.742	1
0	0	2	3.633	3.1	3.607	3.0	3.586	7
1	0	2	3.353	1.0	3.324		3.316	
2	1	0	3.317	2.9	3.324	2.5	3.316	4
*			3.187	1.8				
2	1	1	3.016	10.0	3.020	10.0	3.014	10
1	1	2	2.950	8.7	2.935	5.0	2.929	
3	0	0	2.925	4.3			2.929	8
3	0	1	2.714	0.3	2.721	0.2	2.712	<<1
2	2	0	2.540	0.1	b		2.540	<<1
2	1	2	2.450	1.1	b	2.438	2.440	4
3	1	0						
2	2	1	2.400	0.2	vb		2.395	<<1
3	1	1	2.312	0.6		2.309	2.309	1
3	0	2	2.256	0.1			2.265	<<1
4	0	0	2.193	1.5	b	2.198	2.199	2
1	1	3	2.151	0.1		2.171	2.166	2
4	0	1	2.118	0.3		2.101	2.099	<<1
2	2	2	2.081	2.0		2.077	2.072	2
3	1	2	2.020	1.1	d	2.019	2.016	2
3	2	0						
2	1	3	1.957	3.0		1.944	1.943	8
3	2	1	1.943	2.2		1.944	1.943	8
4	1	0	1.916	1.0		1.919	1.911	1
4	0	2	1.881	1.8		1.876	1.875	3
3	0	3	1.852	0.1			1.853	1
4	1	1						
0	0	4	1.819	0.9		1.802	1.796	2
3	2	2	1.762	0.4	b	1.759	1.756	1
5	0	0						
3	1	3	1.718	0.4	b		1.704	<1
5	0	1						
4	1	2					1.687	<<1
3	3	0					1.687	<<1
4	2	0	1.662	0.5			1.658	<1
3	3	1	1.649	0.7		1.648	1.641	2
4	0	3	1.623	0.1	b		1.614	<<1
4	2	1						
5	0	2	1.596	0.4		1.583	1.575	2
5	1	0						
3	2	3	1.544	1.8		1.543	1.538	3
5	1	1						

Table 1.: X-ray powder diffraction data of two arsenate samples from Nežilovo compared with hedyphane from Långban, Sweden (ROUSE et al., 1984). Legend: b-broad line; vb-very broad line; d-diffuse line; *-plagioclase reflections; d_{hkl} -in Å. Intensities for hedyphane from Långban is given as in ROUSE et al., (1984).

synthetic standards for Cl, Pb and Sr. Operating voltage was 15 kV and sample current 10 nA.

Infra red absorption powder spectra were recorded on Perkin-Elmer IR 398 in the 4000 to 400 cm^{-1} range of wave numbers, using KBr pellets with sample to KBr ratio 1:100.

3. RESULTS

X-ray powder diffraction data of samples are presented in table 1.

On the basis of 32 chosen reflections hexagonal unit cells were calculated and compared with the previously reported data (table 2).

	<i>a</i>	<i>c</i>
Pb ₅ (AsO ₄) ₃ Cl (KREIDLER & HUMMEL, 1970)	10.24	7.44
Sample I, Nežilovo	10.157 (3)	7.256 (6)
Sample II, Nežilovo	10.154 (2)	7.191 (3)
Nežilovo (JANČEV, 1984)	10.150 (14)	7.296 (14)
Långban (ROUSE et al., 1984)	10.140 (3)	7.185 (4)
Turneaureite (DUNN et al., 1985)	9.810 (4)	6.868 (4)

Table 2: Unit cell dimensions of hedyphane and related arsenates from various occurrences (in Å).

Element	SAMPLE I		SAMPLE II	
	%	apfu	%	apfu
PbO	64.93	7.35	60.89	6.54
CaO	5.74	2.59	8.06	3.45
SrO	0.25	0.06	0.07	0.02
As ₂ O ₅	25.85	5.69	27.54	5.74
Cl	2.60	1.85	2.71	1.83
O=Cl-	-0.59		-0.61	
Sum	98.78		98.66	

	SAMPLE I		SAMPLE II	
	n (cm ⁻¹)	I	n (cm ⁻¹)	I
3450	w	3440	m	
1630	vw	1630	vw	
1440	m	1450	vw	
1175	w	1184	s	
1115	vw	1128	s	
1082	m	1091	s	
1045	vw	1030	w	
991	w	988	w	
960	m	968	w	
853	vs	863	vs	
835	s			
827	vs	830	vs	
799	vs	806	vs	
610	w	640	s	
578	w	618	s	
440	vs	449	vs	
385	vs	395	vs	

Table 3: The average values of micro-probe analyses of sample I (4 point analyses) and sample II (3 point analyses). Formula units are calculated on the basis of 10 cation positions. Legend: % - wt. percentage; apfu-atoms per formula unit.

Both electron microprobe analyses (table 3) gave formula with ratio Pb:Ca of about 6:4 what is in agreement with definition of hedyphane after ROUSE et al. (1984).

On the basis of chemical analyses and unit cell dimensions calculated density of sample I is 6.43 gcm⁻³, and the sample II is 6.15 gcm⁻³.

Calculations according to Gladstone-Dale formula gave mean refractive index for the first mineral $n = 1.96$, and for second one $n = 1.93$.

Infrared absorption spectra (table 4) suggest that there are some water incorporated in apatite structure of both arsenates (medium absorption band at 3450 cm⁻¹ and very weak one at 1630 cm⁻¹).

4. DISCUSSION

Hedyphane was reported as (Pb,Ca)₅(AsO₄)₃Cl (PALACHE & al., 1951), but later it is defined as lead-calcium arsenate with Pb:Ca ratio close to 6:4 (ROUSE et al., 1984). JANČEV (1984) described hedyphane from Nežilovo and gave its X-ray pattern and partial chemical analysis. Recently among the Nežilovo samples two distinct members of lead-calcium arsenate isomorphic series were found.

We use the name hedyphane for the specimens from Nežilovo based on the requirements set by ROUSE et al. (1984) "that Pb and Ca be major elements having a molar ratio of about 3:2, that As exceed P and Cl

Table 4: IR spectra of arsenate samples from Nežilovo. Legend: vw-very weak; w-weak; m-medium; s-strong; vs-very strong.

exceed F or OH". The authors have also identified hedyphane as an ordered phase in the series between turneaureite, Ca₅(AsO₄)₃Cl and mimetite Pb₅(AsO₄)₃Cl.

Our study did not include determination of the degree of ordering of Ca and Pb atoms. However, based on the chemical composition (Table 3) we classify the two specimens from Nežilovo as hedyphane; their Pb:Ca ratios of 7.35:2.59 and 6.54:3.45 are closer to hedyphane than to any other member of the apatite group.

The intensities of the reflections in XRD powder pattern are different due to considerably different Pb:Ca ratio; patterns were indexed after ROUSE et al. (1984). Calculations for intensities manipulating with different Pb:Ca ratios gave considerably different results in agreement with our measurements (Table 1).

The most important is substitution of Pb by Ca, but there is much more Sr in arsenate rich in lead (sample I). The other arsenate (sample II) is much closer to hedyphane defined by ROUSE et al. (1984). Both samples are chemically homogeneous, what means that they grew at stable conditions.

Differences in calculated mean refractive indices and calculated densities between this two minerals could be explained by higher content of Pb in one (7.35 Pb apfu) than in another (6.54 apfu) arsenate.

Absorption bands in IR of both arsenate samples at about 3450 cm^{-1} could be attributed to hydroxyl vibrations. This hydroxyl group probably substitute some chlorine as additional anion. Very weak absorption at 1630 cm^{-1} is most likely result of some water molecule bending.

This study show that there are not even traces of Ba in both samples. There are two possible explanations for that feature: 1) it could be that Ba was introduced later in that occurrence than arsenate; 2) it is possible that Ba had restricted migrability when the arsenates crystallized. These conditions are indicated by the presence of magnetoplumbite and arsenate apatites.

Magnetoplumbite, $(\text{Pb}_{0.99}\text{Ca}_{0.01})(\text{Fe}_{6.12}\text{Mn}_{2.53}\text{Zn}_{1.89}\text{Al}_{1.03}\text{Ti}_{0.41}\text{Mg}_{0.02})\text{O}_{17.78}(\text{OH})_{0.94}$, where Mn and Fe are in a trivalent state (BERMANEC et al., 1993; BERMANEC & ŠČAVNIČAR, 1993) is one of numerous rare mineral from Nežilovo paragenesis (together with cymrite, tilasite, ardennite...). Arsenate-apatite is additional support for assuming that the crystallization conditions were highly oxidizing. Barium in such circumstances has restricted migrability. This may be the reason why, in spite of possible substitution of barium for lead in this structure (DUNN & ROUSE, 1978) and in spite of high barium positive anomaly in Nežilovo (if it existed at the time of arsenates crystallization), there is no traces of barium in hedyphane samples.

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