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Solid Solution Between Epidote and Hancockite from Nežilovo, Macedonia

Simeon **JANČEV**[1] and Vladimir **BERMANEC**[2]

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Abstract

A solid solution between the epidote formula and hancockite formula (Pb equivalent of epidote) was found in the "mixed series" of the Pre-cambrian complex in the central part of the Pelagonian massif near the village of Nežilovo. The mineral is determined by optical investigation, X-ray diffraction and microprobe analyses. A thermogravimetric analysis was performed and determined 1.68 wt.% of H_2O. Two distinct compositions were found: one with 20-25 mol% and one with about 70 mol% of hancockite component, indicating two different parageneses where the Ca in epidote is partly substituted by Pb.

1. INTRODUCTION

Hancockite, $CaPbAl_2Fe(SiO_4)(Si_2O_7)O(OH)$ is a rare member of the epidote group minerals, first discovered at Franklin, New Jersey (PENFIELD & WARREN, 1899) and later at Jakobsberg, Filipstad, Sweden (HOLTSTAM & LANGHOF, 1994) and at Nežilovo, Macedonia (JANČEV, 1997),

The "mixed series" in the upper part of the Babuna river, near the village of Nežilovo, Macedonia is well known as a region of a positive geochemical anomaly for a variety of elements (Ba, Pb, Zn, Mn, As and REE). Many rare minerals were detected in studies of the minerals and rocks from Nežilovo, including: cymrite (JANČEV, 1975), piemontite (BARIĆ, 1960; JANČEV, 1990; BERMANEC et al., 1994), tilasite (JANČEV, 1984a; BERMANEC, 1994), hedyphane (JANČEV, 1984b; BERMANEC et al., 1993) and nežilovite (BERMANEC et al., 1997), hancockite and Zn-rich aegirine-augite (JANČEV, 1997).

Faculty of Technology and Metallurgy, "Sv. Kiril i Metodij" University, 91000 Skopje, Macedonia.

Faculty of Science, University of Zagreb, Institute of Mineralogy and Petrography, Horvatovac bb, HR-10000 Zagreb, Croatia.

A study of such an unusual locality should improve the knowledge of such peculiar parageneses and about the metamorphic processes generally. It is also of scientific interest to broaden our knowledge about the crystallochemical characteristics of the epidote group minerals.

2. OPTICAL INVESTIGATIONS

It is easy to distinguish two types of Pb-containing epidote group minerals in microscopic thin sections of the Nežilovo rocks. One type is greenish-yellow, displaying columnar crystals up to 0.3 mm in size. Idiomorphic crystals are penetrated by very fine grained hematite inclusions. Cleavage is not obvious. Colour is homogeneous (Fig. 1). This type is located inside the lenses accommodating quartz, mica, barite and hematite. Lenses are enclosed within the barite-schists.

Another type is located within the fine grained quartz veinlets. Hipidiomorphic grains are up to 0.1 mm in size, clear and homogeneous. Sometimes, cleavage is visible (Fig. 2).

The colour is greenish-yellow with pleochroism: yellow - perpendicular to elongation and green - parallel to elongation.

3. CRYSTAL CHEMISTRY

The epidote-hancockite isomorphous series is found at Nežilovo. Electron microprobe analyses clearly indicate two distinct Ca/Pb ratios. Eighteen point analyses were performed on randomly selected grains and there was no significant zonation (Table 1), supporting optical homogeneity. It is possible to distinguish a group of mineral grains with lower and higher Pb-contents. The lower Pb-content was analysed in a group of bigger grains with 20-25 mol% hancockite. The higher Pb-contents originated from a group of smaller grains with an average of 70 mol% hancockite. Higher contents have smaller grains, placed in fine-grained quartz veinlets.

Analysis "han20" is an average of two analyses. The composition of this mineral deviates significantly from other analyses toward the Mn end-member as in the case of Pb- and REE-rich piemontite from the same locality (BERMANEC et al., 1994).

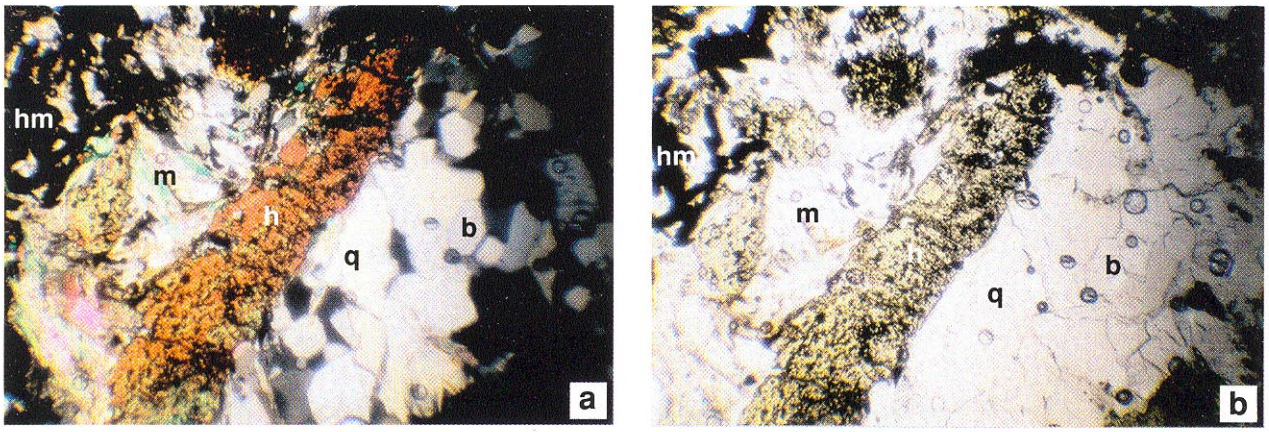

Fig. 1 Fine-grained (ca 0.2-0.3 mm) yellowish-greenish columnar elongated hancockite (h) crystal fulfilled by fine-grained hematite inclusions in a frame of lens-like quartz (q) - mica (m) - baryte (b) - hematite (hm) body enclosed in baryte schists. a) N+; b) N-.

Although it was not possible to separate pure material for water determination (the mineral was mixed with quartz or/and with hematite), one thermogravimetric analysis was performed. The obtained value of approximately 1.68 wt% H_2O is close to the expected amount. However, this value was not used in calculation of the formula.

Observed chemical contents of minerals in Nežilovo deviate from the investigated hancockite from Jakobsberg (HOLTSTAM & LANGHOF, 1994) and Franklin (DUNN, 1985). The most prominent difference between the sample from Nežilovo and samples from Franklin is that in the Nežilovo sample there is no Sr and the Mn content is 3-7 times lower. Only the sample from Jakobsberg contains Ba and its Mn content is similar to samples from Nežilovo.

Another very important difference is that there is an obvious isomorphous substitution of Fe for Mn (Table 1). Such a prominent deviation from the ideal hancockite end-member composition shows that solid solutions between epidote and hancockite could be extended to a third end-member in the group - hypothetical "lead-manganese epidote", $CaPbAl_2Mn(SiO_4)(Si_2O_7)O(OH)$. It is very likely that such an end-member will be found after detailed investigation in the Nežilovo area. It is necessary to collect more Mn-rich samples (e.g. those used for analysis "han20" in Table 1) to investigate this part of the solid solutions in the epidote group. This analysis could also be interpreted in terms that some Mn substitutes for Ca, as proposed by BONAZZI et al. (1990).

4. X-RAY INVESTIGATION

X-ray powder diffraction shows good agreement with the hancockite diffraction pattern of a sample from Franklin, NJ (JCPDS 17-212). The diffraction pattern of hancockite from Nežilovo is contaminated with barite, quartz and hematite lines, due to poor separation. Better separation is not possible due to the numerous inclusions. However, the diffraction pattern is good enough to be indexed and to calculate unit cell dimensions. Unit cell dimensions for hancockite samples are compared in Table 2.

Decreasing *b* and increasing *a* and *c* edges of the unit cell in hancockite (compared with piemontite and alanite) is influenced by substitution of Pb (1.35Å) for Ca (0.99Å) in the elastic epidote structure.

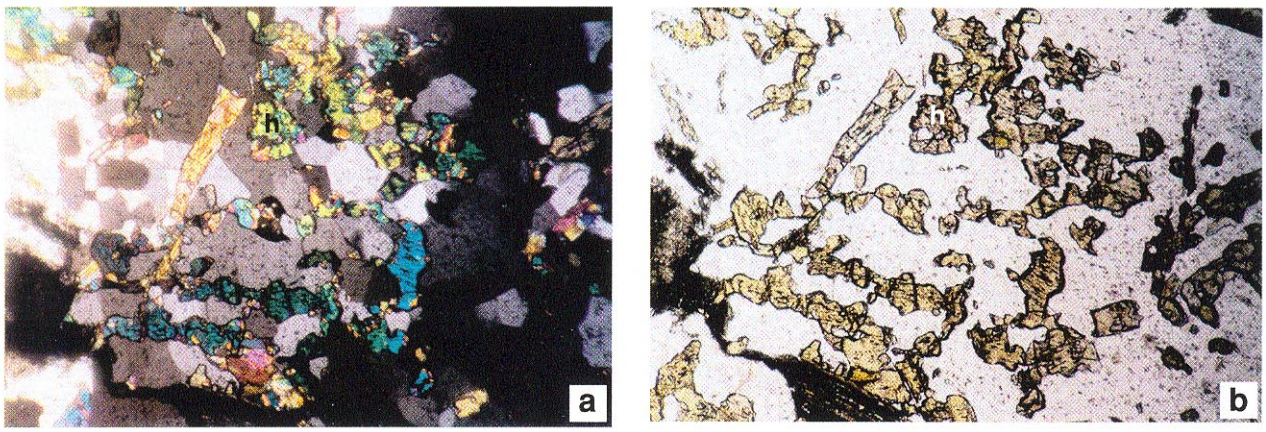

Fig. 2 Fine-grained (ca 0.1 mm) hancockite (h) crystal enclosed in veinlets of fine-grained quartz groundmass. a) N+; b) N-.

No	han2	han3	han15	han17	han20	
SiO_2	34.62	35.47	28.79	28.58	31.33	
Al_2O_3	20.25	20.65	18.10	17.77	10.73	
Fe_2O_3	15.19	15.53	13.05	13.77	10.53	
Mn_2O_3	0.49	0.50	0.88	0.88	9.26	
PbO	10.04	10.26	26.81	25.99	23.48	
CaO	18.96	19.42	11.99	12.34	14.80	
TOTAL	**101.23**	**101.83**	**99.62**	**99.33**	**100.13**	
Si	3.01	3.01	2.87	2.83	2.82	3.00*
Al	2.07	2.06	2.13	2.07	1.14	1.21
Fe^{3+}	0.99	0.99	0.98	1.02	0.71	0.76
Mn^{3+}	0.03	0.03	0.07	0.07	0.64	0.67
Pb	0.23	0.23	0.72	0.69	0.57	0.60
Ca	1.76	1.77	1.28	1.31	1.43	1.52
					Pb+Ca =2.00	Si =3.00

Table 1 Representative electron microprobe analyses of the hancockite-epidote series from Nežilovo.

	a(Å)	b(Å)	c(Å)	β(°)
Franklin (JCPS17-212)	9.03	5.62	10.29	115.93
Franklin (DOLLASE, 1971)	8.96 (2)	5.66 (1)	10.30 (2)	114.4 (4)
Nežilovo	8.98 (1)	5.65 (1)	10.31 (3)	115.4 (2)
Pb & REE-rich piemontite Nežilovo (BERMANEC et al., 1994)	8.880 (1)	5.681 (1)	10.166 (3)	114.66 (2)

Table 2 Unit cell dimensions of hancockite from Nežilovo and related minerals.

5. CONCLUSION

Two distinct members of solid solutions between epidote and hancockite are identified in the Nežilovo region. The present investigation shows that there is a possibility of a high range of substitution of Mn^{3+} for Fe^{3+} in the same system towards the piemontite equivalent of hancockite. Such a phase approaching the $PbCaMn^{3+}Al_2Si_3O_{12}(OH)$ "end member" deserves further investigations, as it is poorly described in prior work. The very unusual paragenesis which is not described completely provides scope for the discovery of a further end member.

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