

THE ASSOCIATION OF OXYGEN-BEARING MINERALS OF CHALCOPHILE ELEMENTS IN THE OROGENETIC ZONE RELATED TO THE “MIXED SERIES” COMPLEX NEAR NEŽILOVO, REPUBLIC OF MACEDONIA ♦

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New data are obtained for minerals from metasomatic rocks of the orogenic zone related to the “Mixed series” metamorphic complex situated in the Pelagonian massif near the Nežilovo village, about 40 km SW of Veles, Republic of Macedonia. A specific feature of these rocks is the concentration of chalcophile elements (S, As, Sb, Zn, Pb) mainly in the form of oxides and oxysalts, whereas sulfides and sulfosalts are present only in trace amounts. Rock-forming and accessory minerals have been characterized by electron microscopy, electron microprobe analyses and in part by X-ray diffraction and IR spectroscopic data. Some of described minerals (Sb-rich analogue of zincohögbomite-2N6S, hydroxyplumbobetafite, Fe³⁺-analogue of coronadite) are potentially new mineral species. Some genetic aspects of the formation of oxidized As-Sb-Zn-Pb-rich rocks are discussed.

Keywords: chalcophile elements; minerals; “Mixed series”; Nežilovo; Pelagonian massif

АСОЦИЈАЦИЈА НА МИНЕРАЛИ ОД ХАЛКОФИЛНИ ЕЛЕМЕНТИ ШТО СОДРЖАТ КИСЛОРОД ВО ОРОГЕНЕТСКАТА ЗОНА ОД КОМПЛЕКСОТ “МЕШАНИ СЕРИИ” БЛИЗУ НЕЖИЛОВО, РЕПУБЛИКА МАКЕДОНИЈА

Добиени се нови податоци за минералите во метасоматските карпи на орогенетската зона од метаморфниот комплекс „мешана серија“ во пелагонискиот масив близу селото Нежилово, околу 40 км југозападно од Велес, Република Македонија. Специфична карактеристика на овие карпи е концентрацијата на халкофилните елементи (S, As, Sb, Zn, Pb), кои се јавуваат главно во форма на оксиди и оксосоли, додека сулфидите и сулфосолите се присутни само во траги. Минералите од кои се формирани карпите и придружните минерали се карактеризирани со помош на електронска микроскопија, рендгенска микроанализа и делумно со рендгенска дифракција и со инфрацрвена спектроскопија. Некои од опишаните минерали (збогатен со Sb аналог на цинкохөгбомит-2N6S, хидроксиплумбобетафит, Fe³⁺-аналог на коронадит) се потенцијално нови минерални примероци. Дискутирани се некои генетски аспекти на формирање оксидирани карпи збогатени со As-Sb-Zn-Pb.

Клучни зборови: халкофилни елементи; минерали; „мешана серија“; Нежилово; пелагониски масив

♦ Dedicated to Academician Gligor Jovanovski on the occasion of his 70th birthday.

1. INTRODUCTION

The famous “Mixed series” metamorphic complex situated in the Pelagonian massif near the Nežilovo village, about 40 km SW of Veles, Republic of Macedonia, is a metamorphosed volcano-sedimentary formation composed mainly of albite augen gneisses and meta-rhyolites around which there are lenses of dolomitic marbles metasomatically replaced by very unusual and complex mineral assemblages [1, 2]. In the footwall of the mentioned dolomitic marbles and barite schists at the Kalugeri Hill, peculiar quartz-cymrite and cymrite-quartz schists are outcropped [3, 4]. Along with cymrite, these rocks contain other Ba-bearing silicates (hyalophane and sanbornite) as accessories.

The metasomatic rocks forming exo-contact aureoles around the high alkaline body of the meta-rhyolites are characterized by variable contents of the main rock-forming minerals (barite, dolomite, quartz, Zn-rich phlogopite, Zn-bearing aegirine-augite, Zn-rich alkaline amphiboles, spessartine, hematite, *etc.*). Specific accessory minerals belonging to this assemblage are gahnite, franklinite, nežilovite, Zn-bearing braunite, zincohögbomite and its Sb-rich variety (or analogue), Zn-rich rinmanite, tilasite, hedyphane, epidote-(Pb), piemontite-(Pb), *etc.* [3–17]. Nežilovo is the type locality of nežilovite, piemontite-(Pb) and zincohögbomite-2N6S.

The mineral associations of these metasomatic rocks are very complex. This shows crystallization within a wide temperature range, starting from the pneumatolytic to the lowest-temperature hydrothermal stages, at high Eh values. One of the most interesting specific features of these metasomatic rocks is the high concentration of several typical chalcophile elements (S, As, Sb, Zn, Pb) forming mainly oxygen-bearing minerals (oxides and oxysalts) among which barite is the major concentrator of sulfur. Sulfide minerals (sphalerite, galena, pyrite and chalcocite) are present there only in trace amounts. Additionally, metacinnabar was detected as a very rare accessory mineral in the fine-grained quartz-barite schists.

In this paper we present new mineralogical data for metasomatic rocks from the orogenic zone related to the “Mixed series” of Nežilovo.

2. ANALYTICAL TECHNIQUES

The EDS-mode electron microprobe analyses, including imaging of the objects in the secondary and backscattered electron (BSE) modes and X-ray microanalysis were performed with two analytical suites, (1) a digital scanning electron

microscope Tescan VEGA-II XMU with energy-dispersive spectrometer (EDS) INCA Energy 450, and (2) a digital scanning electron microscope CamScan MV2300 (VEGA TS 5130MM) with EDS INCA Energy 350. Both electron microscopes are equipped by detectors of secondary and back-scattered electrons on YAG plus an energy-dispersive X-ray microanalyzer with a semi-conducting Link INCA Energy Si (Li) detector. In both cases calculations of results of the X-ray microanalysis were carried out by means of a INCA Energy 300 software package. The analyses were carried out at an accelerating voltage of 20 kV. Current of absorbed electrons on a reference sample of cobalt was 510–520 pA, and on the studied polished samples ranged from 150 to 400 pA (depending on a micro-relief, structure and composition of samples). The size of an electron beam on the sample surface varied in the range 157–180 nm in the analytical mode and up to 60 nm in the scanning mode. The excitation zone reached 4–5 μm . The sample-to-detector distance was 25 mm. BSE imaging was carried out with magnifications from 10 to 2500.

For powder IR absorption spectroscopy, hand-picked grains were grounded in an agate mortar, mixed with anhydrous KBr, pelletized, and analyzed using ALPHA FTIR spectrometer (Bruker Optics) in the range of wavenumbers from 360 to 3800 cm^{-1} , with the resolution of 4 cm^{-1} and the number of scans of 16. The IR spectrum of a pure KBr disk was subtracted from the overall spectrum.

Powder X-ray diffraction studies of minerals were carried out on a Stoe IPDS II single-crystal diffractometer equipped with an image plate detector using the Gandolfi method (MoK α radiation) and on a Rigaku Miniflex II powder diffractometer (CuK α radiation).

3. MINERALS

3.1. Silicates

The main rock-forming silicate minerals in metasomatites of the Nežilovo orogenic zone are amphiboles and trioctahedral mica (phlogopite). Their specific feature is an unusually high content of zinc (up to ~10 wt.% ZnO in amphiboles and up to ~8 wt.% ZnO in micas).

Zn-rich **richterite** and amphiboles belonging to the **magnesioriebeckite–richterite** solid-solution series form yellow, brown or blue-green anhedral grains and split prismatic crystals, as well as their random aggregates embedded in a metasomatic rock (Fig. 1). These minerals crystallized as

Table 1

Representative compositional data for Zn-bearing rock-forming silicate minerals from the Nežilovo orogenic zone

Mineral →	Magnesio-riebeckite	Magnesio-riebeckite	Richterite	Phlogopite	Phlogopite ¹	Aegirine-augite	Spessartine
Constituent	Wt. %						
	1	2	3	4	5	6	7
Na ₂ O	7.38	6.95	7.13	bdl	bdl	7.70	bdl
K ₂ O	bdl ²	bdl	bdl	10.72	10.12	bdl	bdl
CaO	2.37	1.10	3.40	bdl	bdl	1.61	6.41
MgO	13.45	11.51	12.07	22.15	21.03	11.36	0.44
MnO	0.40	bdl	1.92	1.81	1.79	bdl	33.29
FeO ³	–	–	8.67	1.54	1.06	bdl	4.08
ZnO	4.71	7.70	9.34	4.94	7.30	8.03	0.63
Al ₂ O ₃	4.70	4.02	1.65	12.27	12.05	2.01	18.82
Fe ₂ O ₃ ³	10.92	10.92	–	bdl	bdl	13.62	–
TiO ₂	bdl	bdl	bdl	bdl	0.47	bdl	bdl
SiO ₂	54.29	55.98	54.71	41.80	39.81	55.12	36.46
F	bdl	bdl	bdl	1.62	1.81	bdl	bdl
-O=F ₂	–	–	–	-0.68	-0.76	–	–
Total	98.22	98.18	98.89	96.17	95.45	99.45	100.13
Formula coefficients							
Na	2.02	2.01	1.99	–	–	0.56	–
K	–	–	–	1.00	0.96	–	–
Ca	0.36	0.17	0.52	–	–	0.06	0.56
Mg	2.83	2.43	2.59	2.41	2.33	0.63	0.05
Mn	–	–	0.23	0.11	0.11	–	2.29
Fe ²⁺	–	–	1.03	0.10	0.07	–	0.28
Zn	0.50	0.80	0.99	0.27	0.40	0.22	0.04
Al	0.79	0.61	0.28	1.06	1.06	0.09	1.81
Fe ³⁺	1.16	1.23	–	–	–	0.38	–
Ti	–	–	–	–	0.03	–	–
Si	7.68	7.93	7.87	3.05	2.96	2.06	2.97
F	–	–	–	0.37	0.42	–	–
Basis of calculation	13 cations except Na and Ca	13 cations except Na and Ca	13 cations except Na and Ca	7 cations except K	7 cations except K	4 cations	8 cations

Note: ¹Additionally this sample contains 0.77 wt.% CuO corresponding to 0.04 apfu Cu.

²Here and thereafter the mark “bdl” means that the content of corresponding component is below its detection limit.

³The valency of Fe is accepted according to theoretical formulae (except aegirine-augite that contains both Fe²⁺ and Fe³⁺).

a result of a high temperature postmagmatic process, after the crystallization of gahnite, franklinite, and Zn-rich pyroxenes. Typical chemical compositions of the amphiboles are given in Table 1 (analyses 1 to 3).

A typical IR spectrum of Zn-rich magnesioriebeckite (Fig. 2) is similar to that of Zn-free magnesioriebeckite [18], but is characterized by relatively broad and poor-resolved bands which indicates a disordered distribution of cations over structural sites. The bands at 3651 and 3639 cm⁻¹ correspond to OH groups in different coordinations (presumably, MgMgMg and MgMgZn respectively).

Zn-rich amphiboles are rare, but not unique. In particular, magnesioriebeckite with ZnO up to 7.8 wt.%, tremolite with ZnO up to 4.3 wt.%, actinolite with ZnO up to 9.0 wt.% and Mn-analogue

of cummingtonite with ZnO up to 10.8 wt.% have been identified in Zn-enriched metasomatic rocks from Franklin, New Jersey, USA [19]; arfvedsonite from alkali granite of the Puklen complex, Greenland, contains up to 4.7 wt.% ZnO [20].

Zn-bearing **phlogopite** (Table 1, analyses 4 and 5) typically occurs as brown split tabular grains. The content of ZnO is no more than 8 wt.%; Zn-dominant trioctahedral mica (hendricksite) was not found in metasomatic rocks investigated in this work.

Zn-rich **pyroxene** is present as corroded acicular crystals in carbonatized zones as relics of the earliest metasomatic stages [10]. Associated minerals are Sb-rich zincohögbomite, Sb-bearing franklinite, Zn-rich richterite, Zn-rich phlogopite, as well as typical hydrothermal minerals (dolomite,

quartz, albite, barite, tilasite, *etc.*). The composition of Zn-rich pyroxene corresponds to aegirine-augite (Table 1, analysis 6).

Garnet, unlike aegirine-augite, amphiboles and phlogopite, has a rather low capacity to concentrate Zn. As a rule, the contents of ZnO in spessartine from the association with Zn-bearing oxide minerals (gahnite, zincohögbomite, almeidaite) is below 1 wt.% (see analysis 7 in Table 1).

The members of the isomorphous series **piemontite-(Pb) – epidote-(Pb)** and **piemontite-(Pb) – Pb-bearing piemontite** are the main silicates concentrating lead in the Nežilovo orogenic zone. These minerals were described by us in detail earlier [16, 17].

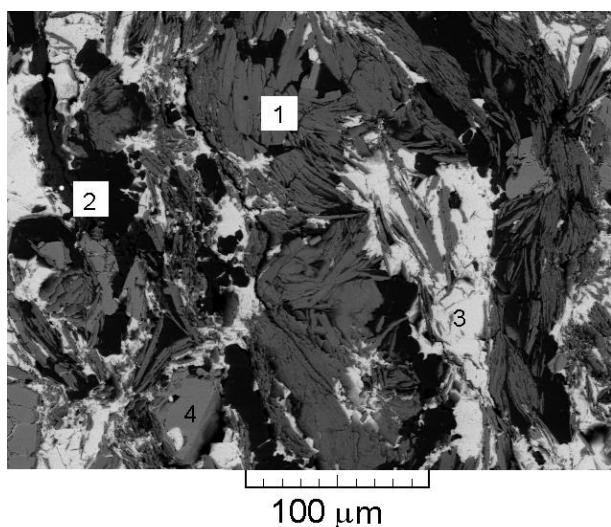


Fig. 1. Aggregates of Sb-bearing zincohögbomite (1), Zn-bearing amphibole (2), barite (3) and hematite (4). Polished section. BSE image.

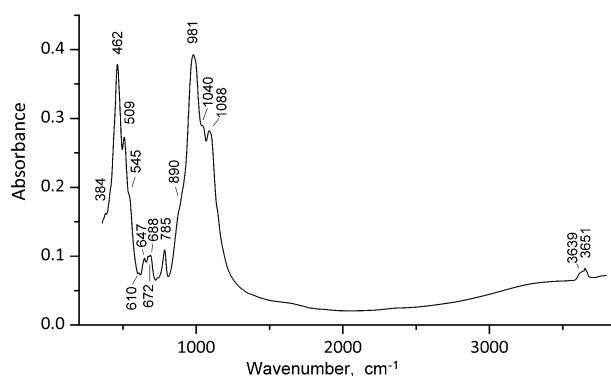


Fig. 2. IR spectrum of Zn-rich magnesioriebeckite.

3.2. Oxides

Oxides are the most abundant and the most diverse accessory minerals in rocks of the Nežilovo orogenic zone and significant concentrators of

chalcophile elements, mainly Pb, Zn and Sb. Most of them belong to the högbomite, crichtonite, spinel and hausmannite groups and to the pyrochlore supergroup. In some associations nežilovite plays an important role as a concentrator of Pb and Zn. Dolomite associated to nežilovite (Fig. 3) is depleted in Zn (the content of ZnO is below 1 wt.%). **Braunite** is present as an accessory component in the dolomite-nežilovite-phlogopite rock (Fig. 1) contains zinc and copper. A typical composition of braunite from this association is (wt.%): CaO 0.78, MgO 1.05, MnO 5.77, ZnO 2.25, CuO 1.62, Al₂O₃ 0.79, Mn₂O₃ 67.54, Fe₂O₃ 11.64, SiO₂ 10.37, total 101.81 (the Mn²⁺ : Mn³⁺ ratio is calculated by stoichiometry); the empirical formula is (Mn²⁺_{0.47}Zn_{0.16}Mg_{0.15}Cu_{0.12}Ca_{0.08})(Mn³⁺_{5.04}Fe³⁺_{0.87}Al_{0.09})Si_{1.02}O₁₂.

Representative analyses of other accessory oxide minerals from metasomatic rocks of the Nežilovo orogenic zone are given in Tables 2 to 4. Specific features of the majority of these minerals are high contents of Zn and/or Sb. In particular, Sb is the main high-valency charge-balancing component in some samples of zincohögbomite-2N6S (analyses 2 and 3 in Table 2; Fig. 1), unlike initially described Sb-, Ti- and Fe-deficient sample from the same locality [15, 21]. Sb-rich zincohögbomite was found in the Nežilovo area by Jančev (2003). It is the first Sb-rich representative of the högbomite, nigerite and taaffeite groups including complex oxide minerals with structures consisting of alternating the spinel-type and the nolanite-type modules [21].

Rinmanite was first described as a mineral from the Garpenberg Norra Zn–Pb mine, Hedemora, Dalarna, Sweden, with the idealized formula Zn₂Sb₂(Mg₂Fe₄)O₁₄(OH)₂ and hexagonal unit cell ($a = 5.9889(4)$, $c = 9.353(1)$, space group $P6_3mc$ [22]). Rinmanite from Nežilovo (analysis 7 in Table 2) differs from type rinmanite in low content of Mg and high content of Zn. Taking into account that Mg does not prevail in any structure sites of rinmanite (and, consequently, Mg is not a species-defining component in this mineral), the samples from Nežilovo represent a new chemical variety of rinmanite.

Almeidaite was discovered recently as a new mineral from Novo Horizonte, Bahia, Brazil [23, 24]. Samples from Nežilovo (analyses 1 and 2 in Table 3) represent the second find of this rare mineral belonging to the crichtonite group. In metasomatic rocks of the “Mixed series” complex almeidaite occurs in association with spessartine and zincohögbomite and forms anhedral grains at the contact of hematite with quartz (Fig. 4).

Table 2

Representative compositional data for accessory oxide minerals from the Nežilovo orogenic zone belonging to the högbomite, spinel and hausmannite groups, as well as rinmanite

Mineral →	Zincohög- bomite- 2N6S	Zincohög- bomite- 2N6S	Zincohög- bomite- 2N6S	Franklinite (?) ¹	Gahnite	Hetaerolite	Rinmanite
Constituent	1	2	3	Wt.% 4	5	6	7
MgO	0.50	bdl	0.78	bdl	bdl	bdl	2.74
MnO	0.31	bdl	bdl	bdl	bdl	–	0.58
ZnO	40.07	40.45	35.31	36.78	44.58	32.12	27.37
Al ₂ O ₃	44.46	43.38	43.56	5.13	53.39	–	3.31
Mn ₂ O ₃	–	–	–	–	–	64.95	–
Fe ₂ O ₃	10.16	10.59	10.88	51.77	2.26	3.59	30.71
TiO ₂	2.39	1.30	1.05	1.49	bdl	bdl	bdl
Sb ₂ O ₅	2.65	4.37	7.32	4.65	bdl	bdl	35.32
Total	100.54	100.09	98.90	99.82	100.23	100.66	100.03
Formula coefficients							
Mg	0.18	–	0.30	–	–	–	0.63
Mn ³⁺	0.06	–	–	–	–	–	0.08
Zn	7.28	7.50	6.64	1.09	1.01	0.94	3.12
Al	12.91	12.80	13.07	0.24	1.94	–	0.61
Mn ³⁺	–	–	–	–	–	1.95	–
Fe ³⁺	1.88	2.00	2.08	1.56	0.05	0.11	3.56
Ti	0.45	0.25	0.21	0.05	–	–	–
Sb ⁵⁺	0.24	0.45	0.70	0.04	–	–	2.02
Basis of calculation	23 cations	23 cations	23 cations	3 cations	3 cations	3 cations	10 cations

Note: ¹Possibly this mineral is the Fe³⁺-analogue of zincohögbomite.

Table 3

Representative compositional data for accessory crichtonite group minerals and nežilovite from the Nežilovo orogenic zone

Mineral →	Almeidaite	Almeidaite ¹	Mn-deficient ana- logue of almeidaite	Nežilovite	Nežilovite
Constituent	1	2	Wt.% 3	4	5
CaO	–	0.24	–	0.38	–
PbO	11.70	11.55	11.86	18.53	19.71
UO ₂	1.32	1.56	–	–	–
MnO	2.43	2.52	1.27	16.42	14.09
ZnO	7.40	7.87	8.23	14.67	13.99
Al ₂ O ₃	–	0.28	–	6.69	5.83
Fe ₂ O ₃	23.69	22.10	23.32	37.65	39.87
TiO ₂	49.86	48.42	49.50	4.24	3.75
ZrO ₂	0.68	0.89	1.73	–	–
Sb ₂ O ₅	2.55	3.20	3.85	0.28	2.06
Total	99.63	98.63	99.76	98.86	99.30
Formula coefficients					
Ca	–	0.09	–	0.08	–
Pb	1.03	1.03	1.04	0.93	1.01
U ⁴⁺	0.09	0.11	–	–	–
Mn ²⁺	0.68	0.72	0.35	2.60	2.28
Zn	1.78	1.94	1.98	2.02	1.97
Al	–	0.11	–	1.47	1.31
Fe ³⁺	5.83	5.55	5.74	5.29	5.73
Ti	12.27	12.16	12.18	0.59	0.54
Zr	0.10	0.15	0.29	–	–
Sb ⁵⁺	0.34	0.39	0.46	0.02	0.15
Basis of calculation	21 cations except Pb and U	21 cations except Pb, Ca and U	21 cations except Pb	13 cations	13 cations

Besides almeidaite *s.s.*, its Mn-deficient analogue (or an analogue of senaite with Fe²⁺ substituting Mn²⁺) has been found in association with hydroxyplumboroméite, zincohögbomite-2N6S, gahnite, hematite, barite, quartz, Zn-rich phlogopite and amphiboles (analysis 3 in Table 3).

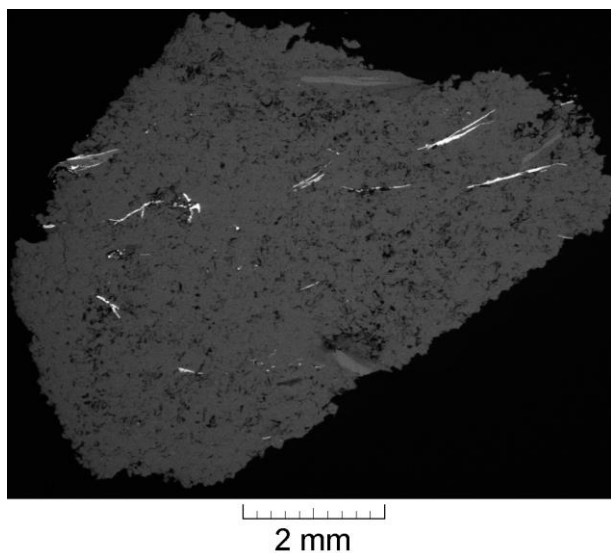


Fig. 3. Nežilovite (white lamellae), Zn-bearing phlogopite (light gray lamellae) and Zn,Cu-bearing braunite (small white grains) in dolomite aggregate. Polished section. BSE image.

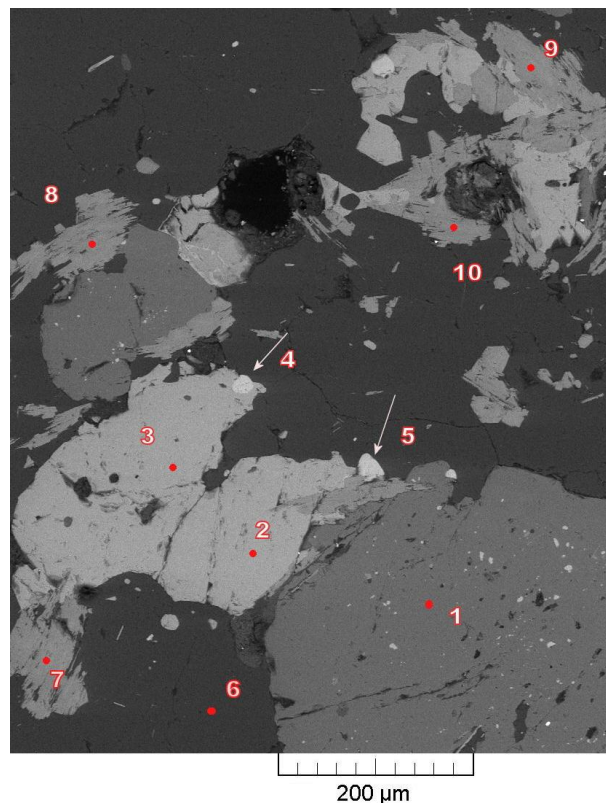


Fig. 4. Association of spessartine (1), hematite (2, 3), almeidaite (4, 5), quartz (6) and zincohögbomite (7-10). Polished section. BSE image.

Table 4

Representative compositional data for accessory pyrochlore-supergroup minerals from the Nežilovo orogenic zone

Mineral →	Hydroxyplumbobetafite	Hydroxyplumboroméite	Hydroxyplumboroméite	Fluorcalcioroméite	Fluorcalcioroméite
Constituent	Wt.%				
	1	2	3	4	5
Na ₂ O	bdl	bdl	bdl	1.76	5.30
CaO	3.82	3.88	7.17	13.11	17.10
PbO	59.01	56.41	45.09	22.19	bdl
Fe ₂ O ₃	bdl	0.90	bdl	bdl	1.53
TiO ₂	14.55	12.03	11.54	12.20	bdl
Sb ₂ O ₅	22.93	25.40	34.89	47.55	75.43
F	bdl	bdl	bdl	2.30	3.52
-O=F ₂	–	–	–	–0.97	–1.48
Total	100.31	100.57	98.67	100.77	101.40
Formula coefficients					
Na	–	–	–	0.25	0.70
Ca	0.42	0.43	0.71	1.05	1.25
Pb	1.63	1.59	1.12	0.44	–
Fe ³⁺	–	0.07	–	–	0.08
Ti	1.13	0.94	0.80	0.68	–
Sb ⁵⁺	0.87	0.99	1.20	1.32	1.92
F	–	–	–	0.54	0.76
Basis of calculation	2 cations Sb+Ti	2 cations Sb+Ti+Fe ³⁺	2 cations Sb+Ti	2 cations Sb+Ti	2 cations Sb+Fe ³⁺

Note: ¹ Additionally this sample contains 2.63 wt.% Ce₂O₃ corresponding to 0.07 apfu Ce.

Accessory pyrochlore-supergroup minerals (members of the roméite and, more rarely, the beta-fite groups) are very diverse in metasomatic rocks of the “Mixed series” complex (Table 4). They form yellow to brown-yellow octahedral crystals up to 0.1 mm and their aggregates. Compositional inhomogeneity is often observed within a single crystal, as zones more or less enriched in Pb, Sb, Na and F (Figs. 5, 6). Both inner and outer zones can be enriched in chalcophile elements: Pb and Sb.

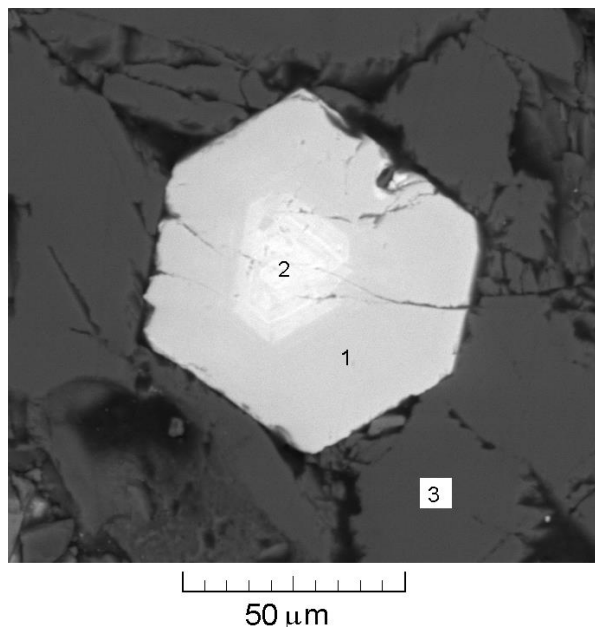


Fig. 5. Pb-poor (1) and Pb-rich (2) fluororoméite forming zones in a crystal embedded in the aggregate of Zn-bearing amphibole. Polished section. BSE image.

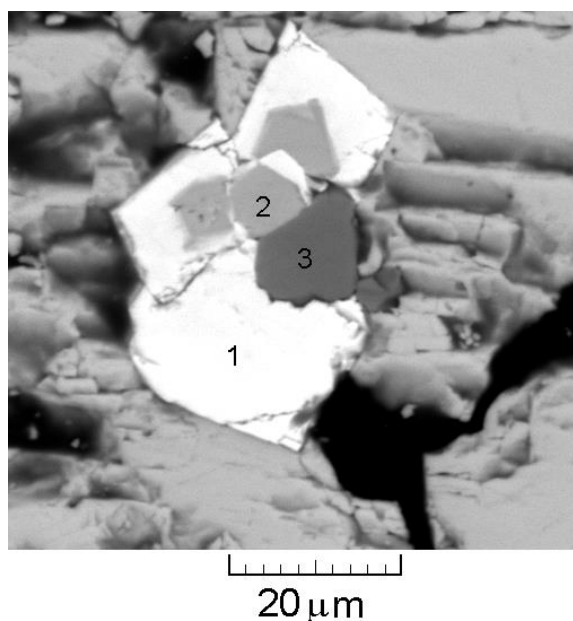


Fig. 6. Intergrowth of hydroxyplumbobetafite (1), fluororoméite (2) and hematite (3) in barite. Polished section. BSE image.

Hydroxyplumbobetafite (Fig. 6, analysis 1 in Table 4) is not approved by the Commission on New Minerals Nomenclature and Classification of the International Mineralogical Association. Moreover, this mineral is not listed among pyrochlore-supergroup species for which analytical evidence is deemed adequate [25]. Consequently, hydroxyplumbobetafite is a potentially new mineral species that needs further investigations.

Högbomite-group minerals are widespread in metasomatic rocks of the Nežilovo orogenic zone [26]. They are characterized by very high contents of Zn and variable contents of Sb. Both Sb-rich and Sb-poor **zincohögbomite-2N6S** form yellow imperfect platy crystals (usually up to 0.1×0.3×0.3 mm) in association with hydroxyplumboroméite, crichtonite-group minerals, gahnite, hematite, barite, quartz, Zn-rich phlogopite and amphiboles. Usually crystals of zincohögbomite-2N6S are split to form aggregates of lamellar blocks sub-coplanar to the *ab* plane and resembling open book in a cross section. The mineral was determined by us as zincohögbomite-2N6S, but not as any other zincohögbomite species based on both electron probe and powder X-ray diffraction data (Table 5).

Table 5

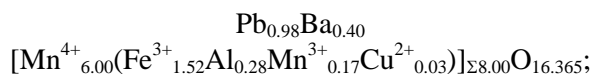
Powder X-ray diffraction data of Sb-rich zincohögbomite-2N6S from Nežilovo.

I_{obs}	d_{obs} (Å)	hkl^*
2	4.77	102
1	4.34	104
5	2.969	1.0.10
32	2.871	110
15	2.776	1.0.11
1	2.640	1.0.12
15	2.472	201
100	2.451	202, 118, 203
5	2.406	204
1	2.321	1.0.14
3	2.306	206
3	2.052	2.0.10
2	1.981	2.0.11
4	1.863	211, 212, 0.0.20
4	1.672	2.1.10
10	1.659	1.0.21
6	1.645	300, 2.1.11, 2.0.17
3	1.585	306, 1.0.22, 2.0.18
30	1.566	2.1.13
28	1.559	308
5	1.534	2.0.19, 1.0.23, 2.1.14
37	1.436	2.0.21, 220, 222

* Indexes *hkl* were chosen taking into account intensities of reflections in the XRD powder pattern calculated from the crystal structure data of zincohögbomite-2N6S (Armbruster *et al.*, 1998).

The hexagonal unit cell dimensions of our Sb-rich zincohögbomite-2N6S, calculated from these powder-diffraction data, are: $a = 5.736(2)$, $c = 36.98(2)$ Å and $V = 1054(1)$ Å³, that is similar to the data for the structurally studied Sb-free zincohögbomite-2N6S, with the empirical formula $Zn_{12.74}(Mg_{0.43}Fe_2Ti_{1.56}Al_{5.29})Al_{24}O_{62}(OH)_2$, from Nežilovo reported in [15]: $a = 5.729(2)$, $c = 37.097(5)$ Å and $V = 1054.45$ Å³.

In some areas fine-grained rocks (with mean sizes of grains *ca.* 0.05–0.1 mm) enriched in franklinite are intersected by hydrothermal veinlets 1–2 mm thick almost completely composed of a coronadite-group mineral. Its empirical formula is



the strongest lines of the powder X-ray diffraction pattern [d , Å (I , %)] are: 3.47 (60), 3.10 (100), 2.43 (90), 2.204 (15), 2.174 (10). This mineral needs further investigations. According to the approved nomenclature of the hollandite supergroup (IMA 11-F; see [27]), it should be named **ferricoronadite**.

3.3. Arsenates

The most common arsenic-bearing minerals in metasomatic rocks related to the “Mixed series” are arsenates (mainly, tilasite and hedyphane [6, 7, 14]; Table 6).

Tilasite was discovered in dolomitic marbles in forms of veinlets characterized with a very complex mineral paragenesis composed of barite, tilasite, Zn-rich aegirine-augite, Zn-rich richterite, Zn-rich magnesioriebeckite, Zn-rich phlogopite, Pb-bearing piemontite, gahnite, quartz, dolomite, roméite-group minerals, hetaerolite, *etc.* On the hydrothermal stage, the older rocks containing fine-grained gahnite, Zn-rich aegirine-augite and Zn-rich amphiboles were metasomatically replaced with the younger coarse-grained rock enriched in barite and/or dolomite and containing tilasite. Accessory tilasite and As-bearing fluorapatite (analyses 1, 4, 5 in Table 6) occur in barite schists in association with barite, Zn-rich amphiboles, Zn-rich rinmanite, gahnite, franklinite, hetaerolite, braunite, *etc.*

Grains of the minerals belonging to the **mimetite-hedyphane** solid-solution series are disseminated in polymictic aggregates (composed of hedyphane, quartz, barite, albite and biotite) forming veinlets up to 3–5 mm thick in dolomitic fine-grained marbles. Accessory mimetite and hedyphane (analyses 2 and 3 in Table 6) occur in metasomatites in association with barite, Zn-rich amphiboles, Zn-rich phlogopite, As-bearing fluorapatite, zincohögbomite-2N6S, *etc.* It is remarkable that As-bearing fluorapatite associated with mimetite does not contain Cl.

Table 6

Representative compositional data for As-bearing accessory minerals from the Nežilovo orogenic zone

Mineral →	Tilasite	Mimetite	Hedyphane ¹	As-bearing fluorapatite	As-bearing fluorapatite
Constituent	Wt. %				
	1	2	3	4	5
CaO	23.67	3.54	5.20	49.73	53.01
PbO	bdl	68.35	66.72	bdl	bdl
MgO	18.68	bdl	bdl	bdl	bdl
MnO	0.96	bdl	bdl	0.59	bdl
P ₂ O ₅	1.14	bdl	bdl	32.65	38.45
As ₂ O ₅	50.93	25.46	25.04	14.29	6.74
F	6.96	bdl	bdl	3.00	3.77
Cl	bdl	2.60	2.78	bdl	bdl
-O=(F,Cl) ₂	-2.93	-0.59	-0.63	-1.26	-1.59
Total	99.41	99.36	101.09	99.00	100.38
Formula coefficients					
Ca	0.95	0.85	1.15	4.55	5.01
Pb	–	4.15	3.72	–	–
Mg	1.04	–	–	–	–
Mn	0.03	–	–	0.04	–
P	0.04	–	–	2.36	2.71
As	0.99	3.00	2.71	0.64	0.29
F	0.82	–	–	0.81	0.99
Cl	bdl	0.99	0.98	–	–
Basis of calculation	5 anions	3 atoms As	3 atoms As+V+Fe	3 atoms P+As	3 atoms P+As

Note: ¹Additionally this sample contains 1.06 wt.% Fe₂O₃ and 0.92 wt.% V₂O₅ corresponding to 0.16 apfu Fe³⁺ and 0.13 apfu V⁵⁺.

4. DISCUSSION

Post-magmatic fluids related to meta-rhyolites are considered as a possible source of a number of specific, ore and rare elements (Pb, Zn, Sb, As, Cu, Ba, REE, etc.) in contact-metasomatic rocks widespread in the Nežilovo area [10]. On the earliest stages of the formation of these rocks, high-temperature pneumatolytic processes occurred at conditions of a very high oxygen fugacity. Accessory Zn,Fe,Mn,Cr-spinels, Zn-bearing pyroxene and garnets are the indicators of the earliest stages of metasomatism. Zn,Fe,Mn-spinels of the second generation, nežilovite, zincohögbomite (including its Sb-bearing variety or analogue), Zn-rich rinmanite, epidote-(Pb), piemontite-(Pb), hematite, almeidaite, etc., crystallized on the second stage. During the lowest temperature hydrothermal processes, different coarse-grained and fine-grained rocks enriched in barite, carbonates, quartz and albite and containing accessory arsenates were formed. Hydrothermal sphalerite-galena mineralization is of minor importance and is confined to local zones with minerals formed under low oxygen fugacity.

As it is noted above, specific features of metasomatic rocks from the orogenetic zone related to the "Mixed series" of Nežilovo are high contents of chalcophile elements (S, As, Sb, Zn, Pb) concentrated mainly in oxides and oxysalts, whereas sulfides and sulfosalts are present only in trace amounts. The oxidized ores form lens-shaped bodies at the contact of meta-quartz porphyry and banded microcline schists. Hypothetically, their formation is connected with fluids derived not only from the meta-rhyolites, but also from a deep seated magmatic chamber. This assumption is based on the fact that the magmatic body of the mentioned rhyolites is very small (ca. 1.0×0.8×0.1 km), with a very limited capacity to contribute very complex and widespread mineral parageneses enriched in chalcophile elements.

Based on the regional geological investigations carried out in the time period from 1955 to 1960, the "Mixed series" is a transgressive series formed as a result of a very complex polymetamorphic transformation of marine sediments. Numerous available isotopic $^{32}\text{S}/^{34}\text{S}$ data for barite show that S could be of marine origin. The very complex mineral parageneses of higher temperature stages are often metasomatically replaced with hydrothermal mineral assemblages in which barite quantitatively predominates over all other minerals showing very high barium potential. The presence of cymrite in the rocks underlying dolomitic marbles also indicates a high activity of barium and moderate (250–300 °C) temperatures of crystallization (see [28]). As a result, almost all sulfur becomes fixed in barite that is characterized by a very low solubility and mobility under hydrother-

mal conditions up to 300 °C and 1400 bars [29]. Another possible factor promoting the crystallization of chalcophile elements in the form of oxygen-bearing minerals is caused by high Eh values.

Although the mineral parageneses from the Nežilovo area cannot be compared with anyone in the world, they show some similarities with the well-known Franklin and Sterling Hill zinc deposits in New Jersey, USA. According to W.A. Tarr [30], these deposits were formed as a result of oxidation of initial ore bodies. In the course of these processes sphalerite oxidized, in greater or less degree, to smithsonite or hemimorphite or, rarely, to willemite. The iron sulfide (or sulfides) was oxidized to form hematite or limonite. The rhodochrosite was probably oxidized, in part at least, to manganite, pyrolusite, and braunite. On the next step, the ore bodies have been deeply buried and intensely metamorphosed by heat and pressure. All the minerals in the original rock have been recrystallized. Locally, they are coarsely crystalline aggregates [30].

The famous Långban in Sweden is another example of an endogenic ore deposit containing chalcophile elements solely in form of oxygen-bearing minerals. Some aspects of the origin of this deposit have been discussed by B. Bollmark [31]. Based on chemical analyses of drillcore samples and $^{85}\text{Sr}/^{86}\text{Sr}$ ratios, he concluded that the formation of an ore progenitor sequence was initiated by the exhalation of iron- and manganese-rich solutions of deep-seated origin and possibly of late-stage differentiation. The exhalation presumably took place in aerated sea water, where oxidation occurred. By analogy with the formation of recent hydrothermal submarine Fe-Mn deposits, it could be assumed that P, V, Cu, As, Ba, Pb, etc., were supplied by exhalations [31].

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