
MINERALS
AND MINERAL PARAGENESES

Spinel- and Högbomite-Supergroup Minerals from Sulfide-Free Endogenic Pb–Zn–Sb–As Assemblage in the Pelagonian Massif, Republic of North Macedonia

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Abstract—Sulfide-free mineral assemblages with the chalcophile element minerals from occurrences associated with altered rocks of Pelagonian massif, Republic of North Macedonia have been studied. The inputting sequence of various ore-forming constituents has been revealed on the basis of morphological features, zoning of the spinel-group minerals, and the högbomite supergroup minerals. Conclusions about the inputting consequences of various ore-forming components have shown that these minerals easily form epitaxial and syntaxial intergrowths with each other and with nežilovite due to commensurable unit cell parameters. Some potentially new minerals were identified belonging to the högbomite supergroup.

Keywords: spinel group, gahnite, franklinite, hetaerolite, högbomite supergroup minerals, zincohögbomite, zincovelesite, Pelagonian massif, Republic of North Macedonia

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INTRODUCTION

The altered rocks of the Pelagonian massif in the vicinity of the Nežilovo settlement near Veles, Republic of North Macedonia have high As, Sb, Zn, Pb, and Cu concentrations (Jančev, Chukanov, 2008; Chukanov et al., 2012, 2015, 2016; Jančev., 2016). Unlike most other endogenic assemblages, the chalcophile elements form oxygen-bearing compounds, mainly oxides, silicates, phosphates, and arsenates (Chukanov et al., 2015; Ermolaeva et al., 2016; Varlamov et al., 2017) rather than sulfides and sulfosalts.

This study is focused on the composition of minerals of the högbomite and spinel supergroups (below HSM and spinels, respectively) and their relation to other minerals from a metasomatic ore occurrence related to the so-called Mixed Series located within the Pelagonian massif. In the studied assemblages, zinc spinels (gahnite, franklinite, and hetaerolite) and HSM are abundant and are the major ore constituents.

Structurally, HSM belong to the polysomatic series of trigonal and hexagonal minerals with different lows of regular alternation of spinel (*S*) and nolanite (*N*) modules (Armbruster, 2002). In particular, the periodical unit of the previously reported zincohögbomite-2*N*6*S* from the Palagonian massif (Chukanov et al., 2015) consists of two nolanite and six spinel modules.

In the nomenclature of HSM approved by the Commission on New Minerals, Nomenclature, and Classification (CNMNC) of IMA, the identification of mineral groups (except the taaffeite group) is based on two features: the composition of spinel module and the predominant tetravalent cation in the nolanite module, Ti or Sn. In all HSM known till recently, Al in the spinel model dominates over other trivalent cations (Fe³⁺ and Mn³⁺). A new HSM zincovelesite-6*N*6*S*, Zn₃(Fe³⁺, Mn³⁺, Al, Ti)₈O₁₅(OH) (Chukanov et al., 2017) from the Mixed Series of the Palagonian massif is the first Fe³⁺-dominated member of the högbomite supergroup and therefore it is the parent mineral of the new group of HSM. The periodical unit of this mineral consists of six nolanite and six spinel modules. A detailed study of the compositional variations in HSM from the endogenic sulfide-free Pb–Zn–Sb–As assemblages of the Pelagonian massif showed that the compositional diversity of these minerals is beyond their conventional nomenclature. In particular, Mn⁴⁺ or Sb⁵⁺ can be the major charge-compensating high-valence cations in them.

This study is focused on the compositional variations of HSM and spinels from the sulfide-free occurrences in the vicinity of Nežilovo and their spatial and

genetic relationships both between each other and with other minerals.

SAMPLES AND ANALYTICAL TECHNIQUES

The samples studied represent two assemblages: (1) substantially oxide predominantly composed of the spinel- and ~~hobomite~~ ^{höbomite}-supergroup minerals and (2) substantially silicate, in which zinc spinels and HSM mineral are also important.

Sample FeCor-1 belongs to predominantly oxide (nearly silicate-free) mineral assemblage with extremely high Zn and Pb concentrations and substantial (but subordinate) role of Sb and As. The material was collected in the Babuna Valley at the base of the Kalugeri Hill. Presumably, it comes from dolomite marble (partly replaced by baryte as a result of the alteration process) outcropped at 1070 to 1090 m above sea level. The sample is predominantly composed by gahnite. Zinc spinels (gahnite, franklinite, hetaerolite) and zincovelesite-6N6S are the major rock-forming minerals. Other oxides (hydroxycalcioroméite, almeidaite, Mn analogue of plumboferrite), silicates (zircon, Zn-bearing talc), As-bearing fluorapatite, quartz, and baryte are minor or accessory. The sporadic grains of zincochromite are relics of the earliest paragenetic assemblage (Ermolaeva et al., 2016). Zincovelesite-6N6S occurs as pseudomorphs after Zn-spinels and epitaxial overgrowths on their grains. The sample contains hydrothermal veinlets predominantly composed of ferricoronadite (Chukanov et al., 2016). The other samples studied belong to the silicate assemblage.

Sample Alm-31 collected from the moraine sediments close to the occurrence no. 9 is altered rock composed of predominant granular aggregate of baryte with embedded minerals of silicate assemblage, which are clinopyroxene, amphibole, alkali feldspar, zinc spinels, zincohöbomite-2N6S, and zincovelesite-6N6S. The pyrochlore- and epidote-supergroup minerals, zircon, hematite, almeidaite, and As-bearing fluorapatite are accessories. Zn-bearing talc and quartz are relics of an earlier paragenetic assemblage (Ermolaeva et al., 2016).

Sample Nežilovo-2 consists of predominant dolomite with inclusions of earlier nežilovite, Zn-bearing phlogopite, Zn-bearing talc, gahnite, braunite, and calcite.

Sample Nežilovo-4 consists of baryte, gahnite, Zn-bearing phlogopite, hematite, hollandite, piemontite-(Pb), braunite, and calcite.

Sample Nežilovo-5 consists of braunite with inclusions of baryte, dolomite, hetaerolite, As-bearing fluorapatite, and tilasite.

The studied fragment of Sample 6465 is large quartz grain with inclusions of baryte and zincovelesite-6N6S in association with aggregates of amphibole grains containing numerous embedded grains of

hematite; inclusions of franklinite and gahnite are also present in quartz and amphibole. Another fragment of this sample is hematite–baryte zone containing inclusions of franklinite, As-bearing fluorapatite, and Camimetite intimately contacting with the amphibole zone.

The assemblage of Sample 6467 is similar to that in Sample 6465. Here, baryte–hematite, quartz–baryte, and phlogopite–hematite–gahnite zones are observed. Another fragment of the sample is hematite–baryte zone with Zn-bearing phlogopite and fluorapatite at the contact with large (0.5 mm) grain of piemontite with rutile inclusions. Gahnite is present in all zones.

Sample 6468 is an aggregate of intimately intergrown gahnite and amphibole in baryte.

Sample 6469 is a hematite–gahnite–baryte aggregate with the quartz, Zn-bearing talc, hydroxycalcioroméite, and almeidaite inclusions.

Sample 6470 is composed of baryte with inclusions of Zn-bearing phlogopite, hematite, gahnite, and Zn analogue of melanostibite.

Sample 2017-2 consists of predominant large-cellular baryte aggregate with inclusions of primary Zn-bearing silicates (magnesoribeckite, phlogopite, talc), quartz, hematite, gahnite, zincohöbomite, nežilovite and fine syntaxial intergrown aggregates of zincovelesite-6N6S and nežilovite. The pyrochlore-supergroup minerals (hydroxycalcioroméite and hydroxylplumboroméite) occur there as accessories.

Sample 2017-13 is composed of massive baryte aggregate with relict silicates (Zn-bearing phlogopite, Zn-bearing talc, albite) and quartz. The accessory minerals are hematite, gahnite, Mn⁴⁺ analogue of zincohöbomite-2N6S (Mn⁴⁺ > Ti), and epitaxial intergrowths of zincovelesite-6N6S and nežilovite.

Sample 2017-15 consists of baryte, which contains relict Zn-bearing phlogopite, Zn-bearing talc, and hematite. Abundant gahnite, högbomite-supergroup minerals (zincohöbomite-2N6S, and its Mn⁴⁺ and Sb⁵⁺ analogues), and nežilovite are embedded in baryte.

The chemical composition has been determined on a Tescan Vega-II XMU scanning electron microscope equipped with EDS operated at acceleration voltage of 20 kV and current intensity 400 nA using an INCA Energy 450 system for the registration of the X-ray radiation and calculation of the sample composition. The beam diameter was 157–180 nm (for the determination of the chemical composition) and 60 nm (for the back-scattered electron imaging). Diameter of the propagation zone is not more than 5 μm. The acquisition time is 100 s. The distance from sample to detector is 25 mm. The following standards were used: MgF₂ (F), albite (Na), MgO (Mg), Al₂O₃ (Al), SiO₂ (Si), LaPO₄ (P), FeS₂ (S), NaCl (Cl), sanidine (K), wollastonite (Ca), InAs (As), SrF₂ (Sr), BaF₂ (Ba), REE monophosphates (La, Ce, Pr, Nd, Sm, Eu, Gd,

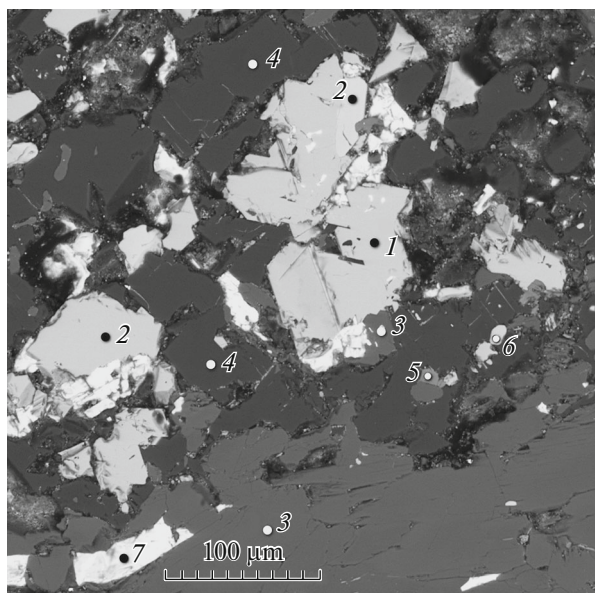


Fig. 1. Back-scattered electron image of (1) franklinite, (2) almeidaite, (3) magnesioriebeckite, (4) albite, (5) As-bearing fluorapatite, (6) zircon, and (7) baryte. Sample Alm-31, polished section.

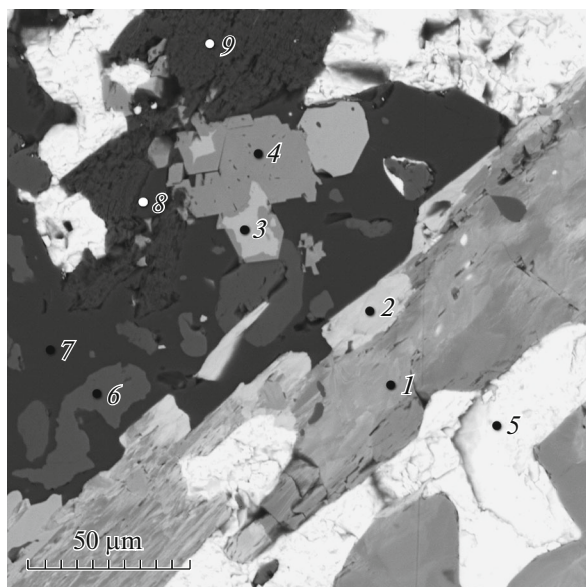


Fig. 2. Back-scattered electron image of (1) piemontite, (2) "ferripiemontite-(Pb)", (3) franklinite, (4) gahnite, (5) baryte, (6) aegirine-augite, (7) albite, (8) quartz, and (9) Zn-bearing talc. Sample 2017-3, polished section.

Tb, Dy, Yb), PbTe (Pb), ThO₂ (Th), UO₂ (U), and pure Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Y, Zr, Nb, Sb, and Hf for corresponding elements.

RESULTS

The spinel supergroup minerals (below spinels) occur as equant grains (Figs. 1, 2), while HSM form near-parallel aggregates of thin lamellas (Figs. 3–9). Gahnite frequently occurs as partial and complete pseudomorphs after franklinite and hetaerolite grains (Ermolaeva et al., 2016; Figs. 2, 4, 5). Zincochromite belongs to the earliest generation of spinels and its relics are occasionally present in the cores of franklinite individuals (Ermolaeva et al., 2016). Regular intergrowths of zinc spinels and the högbomite-supergroup minerals, in which the latter are later, are frequently observed (Figs. 3–7). A presence of the spinel module in the HSM structures is the obvious precondition to form epitaxial HSM on gahnite and franklinite individuals.

Previously it was proven (Chukanov et al., 2015) that zincohögbomite of this assemblage belongs to the polysome 2N6S. Therefore, Sb⁵⁺ and Mn⁴⁺ analogues of this mineral identified in this assemblage and frequently forming zones in the zincohögbomite individuals were presumably referred to the same polysome. However, as reported in (Chukanov et al., 2017), Fe³⁺-dominant member of the högbomite supergroup from the mineralized altered rocks of the Palagomian massif is attributed to polysome 6N6S. On the triangle plot in terms of Al, Mn, and Fe (Fig. 12), the compositions

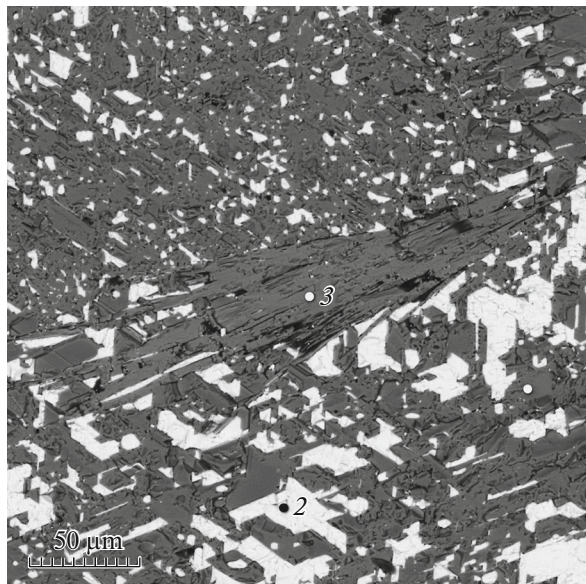


Fig. 3. Back-scattered electron image of graphic intergrowth of (1) gahnite and (2) baryte, and (3) aggregate of zincohögbomite-2N6S crystals. Sample 2017-15, polished section.

fall into two isolated fields. Zincovelesite-6N6S falls into the field with Fe³⁺ > Al, whereas in zincohögbomite Al ≥ Fe³⁺. Thus, it may be assumed that HSM in the structures of which the fraction of the spinel module is 3/4 (the polysome 2N6S) are enriched in Al.

In turn, HSM frequently form intimate epitaxial and syntactic intergrowths with nežilovite (Fig. 8).

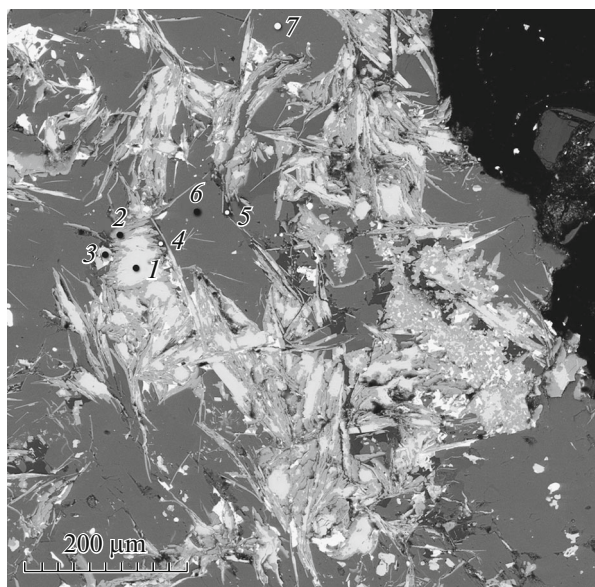


Fig. 4. Back-scattered electron image of (1) franklinite rimmed by (2) gahnite in association with högbomite-super group minerals (cross-sections of platelets), (3) hematite, (4) feldspar, (5) albite, (6) clinopyroxene, and (7) magnesioriebeckite. Sample Alm-31, polished section.

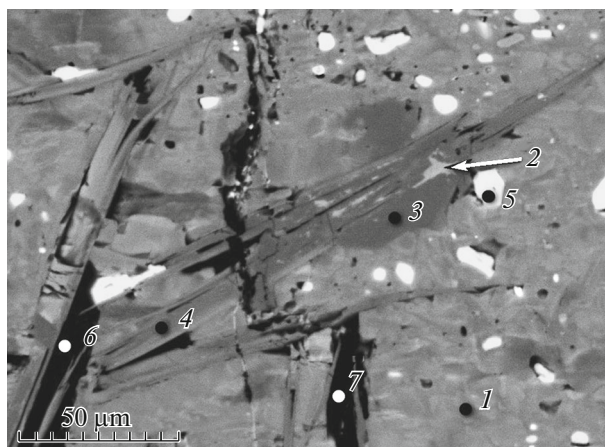


Fig. 5. Back-scattered electron image of (1) piemontite, (2) franklinite, (3) gahnite, (4) zincohögbomite, (5) bar-yte, (6) quartz, and (7) Zn-bearing talc. Sample 2017-3, polished section.

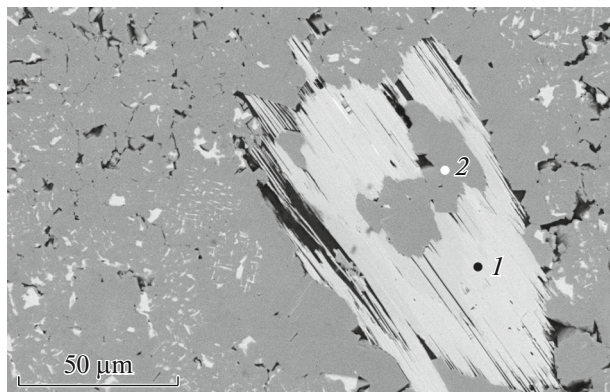


Fig. 6. Back-scattered electron image of (1) zincovelesite-6N6S, (2) gahnite, and (3) franklinite. Sample FeCor-1, polished section.

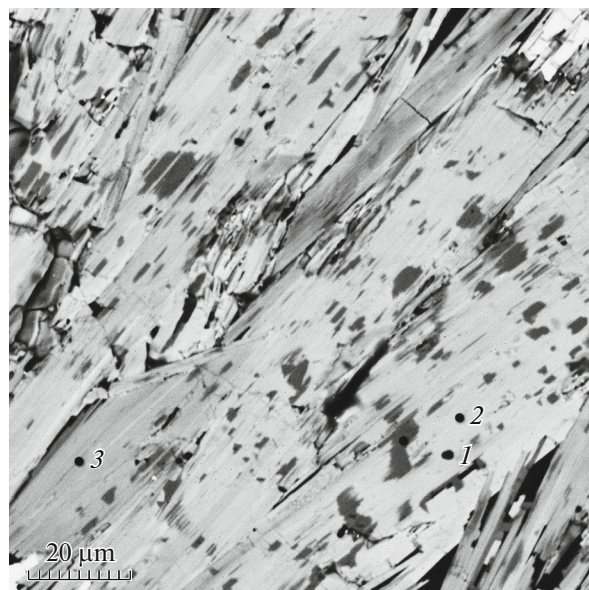


Fig. 7. Back-scattered electron image of (1) relics of gahnite in zoned aggregate of (2) zincovelesite (light zones) and (3) zincohögbomite (dark zones). Sample 2017-2, polished section.

The outer zone of the parallel nežilovite and HSM intergrowths is composed of zincohögbomite that may indicate its late crystallization (later than nežilovite and other högbomite-super group minerals). The latest variety is appeared to be Sb analogue of zincohögbomite (point 1 in Fig. 10). The epitaxy of the högbomite-super group minerals and nežilovite is caused by close a unit cell parameter [5.74 Å for zincohögbomite-2N6S (Chukanov et al., 2015), 5.90 Å for zincovelesite-6N6S (Chukanov et al., 2017), and 5.85 Å for nežilovite (Bermanec et al., 1996)], as well as com-

measurable parameter c for zincovelesite-6N6S (55.87 Å) and nežilovite (22.81 Å).

Most spinel-group minerals in the assemblages studied are extremely rich in Zn (the Zn content is above 0.94 apfu in more than 98% of all compositions). The absence of Mg in spinels and the högbomite-super group minerals can be explained by its incorporation into earlier silicates (amphiboles, pyroxenes, Zn-bearing phlogopite, and talc), as well as into later tilasite and dolomite. Thus, zinc is the only divalent constituent in these minerals, whereas the composi-

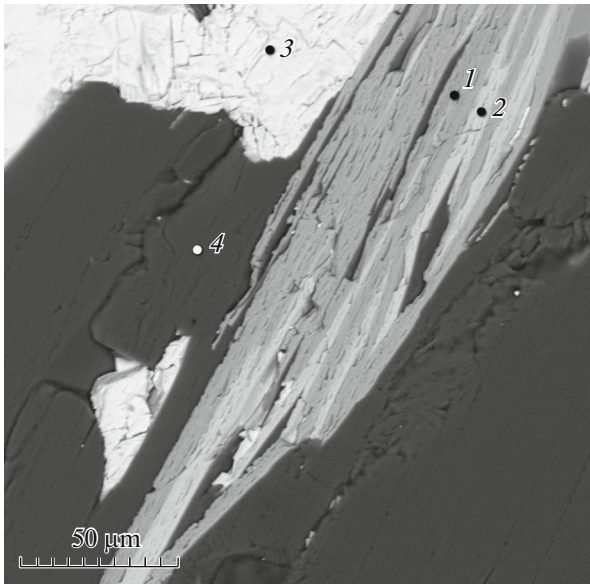


Fig. 8. Back-scattered electron image of syntactic intergrowth of (1) zincovelesite-6N6S with (2) nežilovite in aggregate of (3) baryte and (4) Zn-bearing phlogopite. Sample 2017-13, polished section.

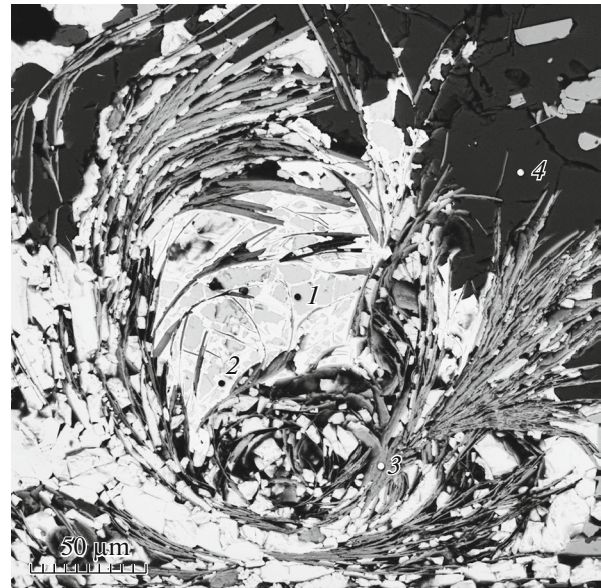


Fig. 9. Back-scattered electron image of aggregate of (1) baryte, (2) hydroxylplumboromeite, and (3) högbomite-supergruop minerals in association with (4) Zn-bearing magnesioriebeckite. Sample 2017-3, polished section.

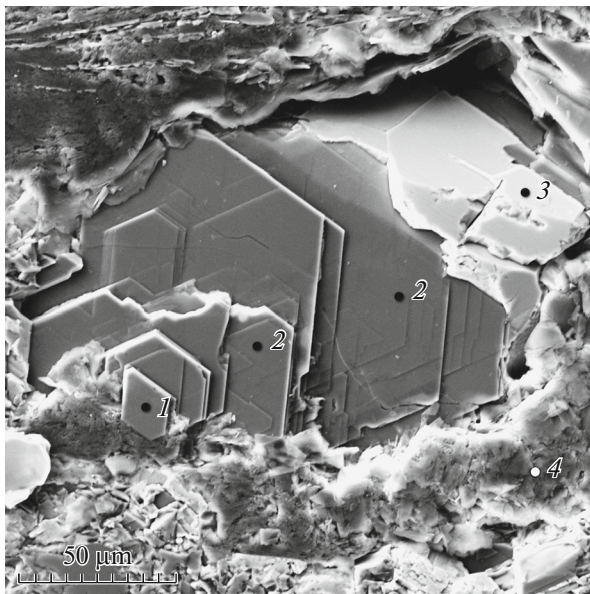


Fig. 10. Back-scattered electron image of (1) Sb analogue of zincohögbomite, (2) zincohögbomite, (3) baryte, and (4) Zn-bearing talc. Sample 2017-15, polished section.

tional variations on them are predominantly associated with trivalent constituents, Al, Fe³⁺ and Mn³⁺ (Tables 1, 2). The triangle plots (Figs. 11, 12) show the relationships of Al, Mn, and Fe in the spinel-group and högbomite-supergruop minerals, respectively. In HSM, the Mn and Fe contents are positively correlated ($r = 0.89$).

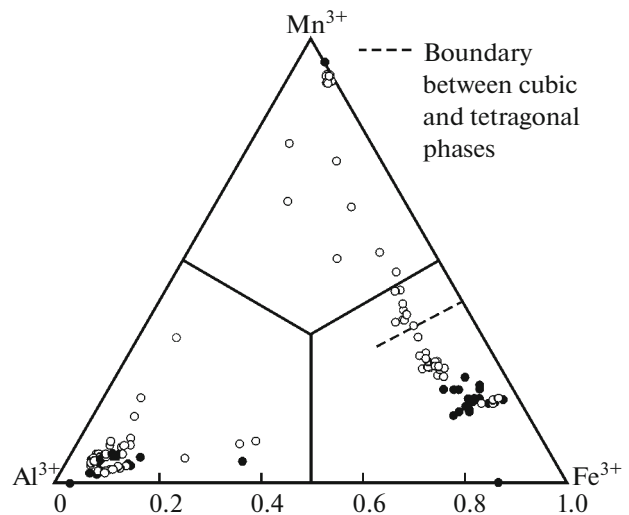


Fig. 11. Triangle diagram illustrating relationships of trivalent cations Al³⁺, Mn³⁺, and Fe³⁺ in zinc spinels (in atomic amounts). Black square (zincchromite) and open circles correspond to samples from the oxide assemblage. Black circles depict samples from the silicate assemblage.

High contents of Zn in associated minerals (up to 0.73 apfu in amphiboles, up to 0.27 apfu in epidote-supergruop minerals, and up to 0.09 apfu in clinopyroxene) and occurrence of Cu (up to 0.14 apfu in epidote-supergruop minerals and up to 0.10 apfu in amphiboles) are of interest (Table 3).

Table 1. Typical chemical compositions of spinels and hetaerolite from occurrences of Pelagonian massif

Component	Gahnite		Franklinite		Hetaerolite		Zincochromite	
	Content, wt %							
CuO	B.d.l.	B.d.l.	0.75	0.48	B.d.l.	B.d.l.	B.d.l.	B.d.l.
MgO	"	0.52	B.d.l.	B.d.l.	"	"	1.00	"
ZnO	44.17	43.88	34.11	33.71	27.51	34.08	35.43	36.94
Mn ₂ O ₃	2.35	1.41	14.19	12.28	9.82	62.37	32.11	1.22
Fe ₂ O ₃	9.26	3.19	48.94	51.86	40.26	5.11	29.30	1.62
Al ₂ O ₃	44.33	51.78	2.74	1.22	15.34	B.d.l.	4.19	10.79
Cr ₂ O ₃	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	"	B.d.l.	49.64
MnO ₂	"	"	1.00	"	6.87	"	0.37	B.d.l.
Sb ₂ O ₃	"	"	B.d.l.	"	2.39	"	B.d.l.	"
Total	100.1	100.78	101.74	99.56	102.18	101.56	102.40	100.21
	Formula coefficients calculated on the basis of 3 cations							
Cu	0	0	0.02	0.01	0	0	0	0
Mg	0	0.02	0	0	0	0	0.06	0
Zn	1.04	0.99	0.98	1.00	0.74	0.99	0.99	1.00
Mn	0.06	0.03	0.42	0.37	0.27	1.86	0.92	0.03
Fe	0.22	0.07	1.42	1.56	1.11	0.15	0.83	0.05
Al	1.68	1.89	0.13	0.06	0.66	0	0.19	0.37
Cr	0	0	0	0	0	0	0	1.45
Ti	0	0	0.03	0	0.19	0	0.01	0
Sb	0	0	0	0	0.03	0	0	0

B.d.l. denotes that the element content is below detection limit by electron microprobe.

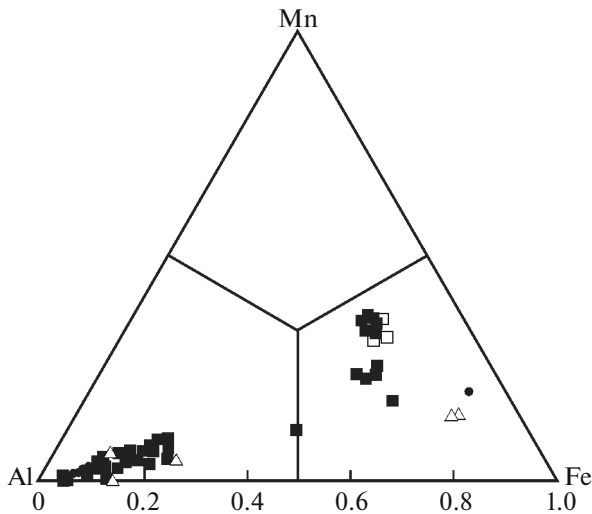


Fig. 12. Triangle diagram illustrating relationships of Al, Mn and Fe in högbomite-supergroup minerals (atomic amounts). Samples from silicate assemblage: Ti > Sb (black squares), Sb > Ti (open triangles), and compositions with atomic contents of Sb + Ti below 2% of the total number of cations (hypothetical members of the högbomite supergroup with species-forming high-valent cation Mn⁴⁺ (black circles). Open squares depict samples from the oxide assemblage with Ti > Sb.

DISCUSSION

Based on the relationships on the mineral phases, the following crystallization sequence of the minerals from the ore-bearing altered rocks of “Mixed Series” of the Pelagonian massif was established: albite + potassium feldspar + Zn-bearing amphiboles + clinopyroxene + Zn bearing phlogopite + hematite + quartz → zincochromite + zircon + Zn-bearing talc + baryte → franklinite + hetaerolite → gahnite → epidote-supergroup minerals + pyrochlore-supergroup minerals + almeidaite → nežilovite + högbomite-supergroup minerals → ferricronadite + Mn analogue of plumboferrite. Zinc spinels belong to an early evolution stage of the altered rocks. The högbomite-supergroup minerals are formed at the later stage (Ermolaeva et al., 2016). Judging from this crystallization sequence, the chalcophile elements were input in the following order: S–Zn–As–Sb–Pb. The high Zn and Cu contents in silicates associated with spinels and HSM indicates that the mineral-forming medium was enriched in these chalcophile elements at an early stage.

As can be seen in Fig. 11, zinc spinels of the gahnite–franklinite–hetaerolite system tend to form predominantly binary solid solutions with minor content of the third component. There are miscibility gaps

Table 2. Typical chemical compositions of högbomite-supergroup minerals from occurrences of Pelagonian massif

Component	Zincohögbomite-2N6S		Assumed Mn ⁴⁺ analogue of zincohögbomite-2N6S		Zincovelesite-6N6S ⁴		
Content, wt %							
CuO	B.d.l.	B.d.l.	B.d.l.	0.16	B.d.l.	B.d.l.	0.50
MgO	"	"	"	1.10	1.00	"	0.97
ZnO	39.47	38.15	38.97	35.82	41.87	25.95	30.80
Mn ₂ O ₃	3.86	6.66	3.41	4.00	2.71	18.01	21.31
Fe ₂ O ₃	7.90	14.17	14.37	15.98	7.07	37.25	29.44
Al ₂ O ₃	44.72	36.05	37.84	31.11	42.99	13.21	8.17
TiO ₂	2.82	2.54	1.93	0.55	1.08	5.57	5.28
Sb ₂ O ₅	2.53	2.30	2.03	7.62	4.57	1.37	3.74
As ₂ O ₅	B.d.l.	B.d.l.	B.d.l.	0.59	B.d.l.	B.d.l.	B.d.l.
Total	101.30	99.87	98.54	96.94	101.28	101.35	100.21
Formula coefficients							
Cu	0	0	0	0.03	0	0	0.05
Mg	0	0	0	0.45	0.37	0	0.20
Zn	7.15	7.27	7.44	7.28	7.65	2.60	3.21
Mn	0.72 ¹	1.30 ²	0.67 ³	0.84	0.51	1.86	2.29
Fe	1.45	2.75	2.79	3.31	1.32	3.79	3.13
Al	12.93	10.97	11.52	10.11	12.53	2.11	1.36
Ti	0.52	0.49	0.38	0.11	0.20	0.57	0.56
Sb	0.23	0.22	0.20	0.78	0.42	0.07	0.20
As	0	0	0	0.09	0	0	0
Total cations	23	23	23	23	23	11	11

The assumed attribution of Mn and Sb analogues of zincohögbomite-2N6S to polysome 2N6S is based on that the powder X-ray diffraction pattern of the previously studied zincohögbomite-2N6S from the Pelagonian massif (Chukanov et al., 2015) was measured from the sample containing zones of these phases. Formulas were calculated on the basis of 23 or 11 cations assuming belonging to polysomes 2N6S and 6N6S, respectively. ¹—including 0.55 apfu Mn³⁺ and 0.17 apfu Mn⁴⁺ (from charge balance constraints); ²—including 0.96 apfu Mn³⁺ and 0.34 apfu Mn⁴⁺ (from charge balance constraints); ³— including 0.01 apfu Mn³⁺ and 0.66 apfu Mn⁴⁺ (from charge balance constraints); ⁴—holotype (Chukanov et al., 2017).

in the intermediate compositional fields of the franklinite–gahnite and hetaerolite–gahnite solid solution series.

It is known that in the franklinite–hetaerolite solid solution series the cubic franklinite structure transits to tetragonal hetaerolite structure at $Fe^{3+} : (Fe^{3+} + Mn^{3+}) = 0.61$ (Mason, 1947). Thus, the compositions of the franklinite–hetaerolite solid solution series within the range of the $Fe^{3+}/(Fe^{3+} + Mn^{3+})$ value from 1 to 0.61 likely correspond to franklinite-*Q* (the tetragonal polymorphic modification of franklinite). Obviously, the partial miscibility of the Al members of the spinel group with their Mn³⁺ and Fe³⁺ analogues and symmetry transformation in the ZnFe₂O₄–ZnMn₂O₄ solid solution series are caused by different ionic radii of Al³⁺ (0.53 Å), Mn³⁺ (0.58 Å), and Fe³⁺ (0.55 Å) (Shannon and Prewitt, 1969).

CONCLUSIONS

The morphological features and zoning of the minerals from the “Mixed Series” occurrences of the Pelagonian massif make it possible to reveal the main input sequence of chalcophile elements: S–Zn–As–Sb–Pb. Spinel and later HSM are the main zinc concentrators. The högbomite-supergroup minerals frequently replace the spinel-group minerals.

There are miscibility gaps between the franklinite and hetaerolite from continuous solid solution series and the franklinite–gahnite and hetaerolite–gahnite solid solution series.

The spinel-group minerals, HSM, and nežilovite easily form epitaxial and syntactic intergrowths that is most likely caused by their commensurable unit cell parameters.

The role of the charge compensating high-valence cation in the högbomite-supergroup minerals can play not only Ti⁴⁺ (Chukanov et al., 2015), but possi-

Table 3. Chemical compositions of oxides associated with spinels and hogbomite-supergroup minerals from occurrences of the Pelagonian massif

Component	Nežilovite	Almeidaite ¹	Min analogue of plumboferrite ²	Ferrocronadite ³	Hydroxycalcioroméite	Hydroxyplumboroméite ⁴	Hydroxyplumbobetafite ⁵	Braunite ⁶
	Content, wt %							
CaO	B.d.l.	B.d.l.	B.d.l.	B.d.l.	10.21	6.39	5.22	0.38
PbO	15.99	11.76	32.29	24.50	28.25	48.77	46.79	B.d.l.
ZnO	16.11	10.00	13.11	0.33	0.17	0.47	B.d.l.	3.23
Fe ₂ O ₃	38.46	15.95	16.84	11.45	0.28	B.d.l.	0.87	6.39
Mn ₂ O ₃	14.61	8.11	23.20	9.90	1.72	"	B.d.l.	80.04
La ₂ O ₃	B.d.l.	B.d.l.	B.d.l.	B.d.l.	0.49	"	0.75	B.d.l.
Ce ₂ O ₃	"	1.41	"	"	8.45	"	3.20	"
Y ₂ O ₃	"	0.30	"	"	0.66	"	0.33	"
Al ₂ O ₃	7.39	0.47	0.71	0.50	B.d.l.	"	B.d.l.	"
TiO ₂	3.86	51.37	16.30	4.19	14.05	11.99	14.80	"
ZrO ₂	B.d.l.	1.39	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	"
Sb ₂ O ₅	2.52	0.83	0.42	"	34.29	31.27	27.88	"
Total	98.95	101.86	103.55	100.84	98.59	100.02	101.44	102.39
	Formula coefficients							
Ca	0	0	0	0	0.93	0.69	0.52	0.04
Pb	0.81	0.98	1.78	1.03	0.61	1.25	1.10	0
Zn	2.25	2.30	1.98	0.04	0.01	0.03	0	0.23
Fe ³⁺	5.47	3.74	2.60	1.35	0.02	0	0.06	0.47
Mn ³⁺	2.10	2.14	3.63	1.18	0.11	0	0	5.99
La	0	0	0	0	0.01	0	0.02	0
Ce	0	0.16	0	0	0.25	0	0.10	0
Y	0	0.05	0	0	0.03	0	0.01	0
Al	1.65	0.17	0.17	0.09	0	0	0	0
Ti	0.05	12.04	2.51	0.49	0.85	0.86	0.97	0
Zr	0	0.21	0.02	0	0	0	0	0
Sb	0.18	0.09	0.03	0	1.02	1.11	0.90	0
Calculation basis	13 cations	22 cations	11 cations except Pb	8 cations except Pb and Ba	Ti + Sb + As + Mn + Fe + Zn = 2	Ti + Sb + As + Mn + Fe + Zn = 2	Ti + Sb + As + Mn + Fe + Zn = 2	8 cations

¹—Total includes 0.26 wt % MgO that corresponds 0.12 apfu Mg (Ermolaeva et al., 2016). ²—High total value are explained by the substantial divalent Mn concentration; also contains 0.67 wt % Nb₂O₅ that corresponds to 0.06 apfu Nb (Ermolaeva et al., 2016). ³—Holotype (Chukanov et al., 2016); also contains 44.81 wt % MnO₂ and 5.16 wt % BaO that corresponds 4.85 apfu Mn⁴⁺ and 0.32 apfu Ba. ⁴—Total includes 1.13 wt % SrO that corresponds 0.06 apfu Sr. ⁵—Total includes 0.19 wt % Pr₂O₃ and 1.42 wt % As₂O₅ that corresponds to 0.01 apfu Pr and 0.06 apfu As. ⁶—Total includes 1.03 wt MgO and 11.32 wt % SiO₂ that corresponds to 0.15 apfu Mg and 1.11 apfu Si.

bly Sb^{5+} and Mn^{4+} . The högbomite-supergroup minerals with Fe^{3+} as the predominant trivalent cation were identified for the first time.

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