

Peculiar antimony-bearing minerals of the spinel group from the metamorphic rocks near Nežilovo village, Macedonia

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Abstract. In continuation of some earlier observations (Jančev, 1993), during the systematic studies of the spinel minerals from the Nežilovo locality, a series of Sb-bearing gahnites and franklinites were established and preliminarily characterized by microscopic examinations and microprobe analyses. There were found:

Sb-bearing gahnite, $Zn(Al,Fe,Sb,Ti,Mn)_2O_4$,

Sb-bearing franklinite, $Zn(Fe,Al,Sb,Ti,Mn)_2O_4$,

Sb-bearing franklinite-hetaerolite $(Zn,Fe)(Fe,Mn,Al,Ti,Sb)_2O_4$, and

antimonoan franklinite $(Zn,Fe)(Fe,Sb,Ti)_2O_4$, a probable new mineral species inside the mentioned group. Further mineralogical studies are in progress.

Key words: gahnite, Sb-bearing gahnite, Sb-bearing franklinite, antimonoan franklinite, Macedonia.

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Янчев С. 2001. Богати на антимон минерали от шпинеловата група в метаморфните скали при с. Нежилово, Македония. – *Геохим., минерал. и петрол.*, **38**, 73-78.

Резюме. В продължение на някои предишни наблюдения (Jančev, 93) при систематичното изследване на шпинеловите минерали от находище Нежилово, са установени серия от Sb-съдържащи гаанити и франклинити, които са характеризирани чрез микроскопски наблюдения и микросондови анализи. Описани са Sb-съдържащ гаанит, Sb-съдържащ франклинит, Sb-съдържащ франклинит-хетеролит и антимонов франклинит $(Zn,Fe)(Fe,Sb,Ti)_2O_4$, вероятен нов минерален вид в шпинеловата група. Понататъшните минераложки изследвания са в ход.

Ключови думи: гаанит, Sb-съдържащ гаанит, Sb-съдържащ франклинит, Sb-ов франклинит, Македония

Introduction

In the frame of a variegated "mixed series" from the metamorphic complex of the Pelagonian massif in Macedonia, there is a peculiar ore bearing zone, consisted of barite, barite-tilasite, quartz-cymrite, hyalophane-cymrite, quartz-hancockite schists, dolomitic marbles, meta-rhyolites and quartzites, originated in volcanic-sedimentary processes and later metamorphosed by polyphase regional-metamorphic events.

The investigated region of the aforementioned series near Nežilovo village in Macedo-

nia, is well known with many rare minerals discovered by different authors, as follows: gahnite and piemontite (Barić, 1960), franklinite (Barić, Ivanov, 1960), cymrite (Jančev, 1975), tilasite and hedyphane (Jančev, 1984), plumboan piemontite (Jančev, 1990), hyalophane, antimony-rich gahnite, zinc-rich phlogopite and zinc-rich richterite (Jančev, 1993), nežilovite (Bermanec et al., 1996), hancockite, zinc-rich aegirine-augite (Jančev, 1997), titanium- and iron-poor zincohögbomite-16H (Armbruster et al., 1998).

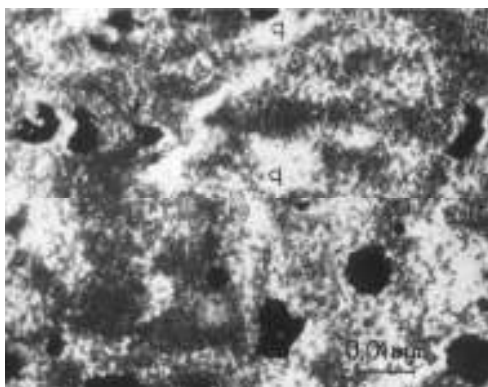


Fig. 1. Fine grained (~ 0.01 mm) inclusions of yellowish-greenish Sb-bearing gahnite in hydrothermal quartz (q) associated with hematite (black). N //

Фиг. 1. Дребнозърнести включения от жълто-зелен Sb-съдържащ гаанит в хидротермален кварц (q), асоцииращ с хематит (черно). N //

According to Mandarino (1999), in the frame of the spinel group, there are no so far reported Sb-rich minerals. But, in addition to the announced earlier Sb-rich gahnite, in the Nežilovo area, we have found some more members of the gahnite-franklinite series with variable, in some cases rather high content of antimony. Here, some analytical data for the chemical composition of these unusual spinels will be presented.

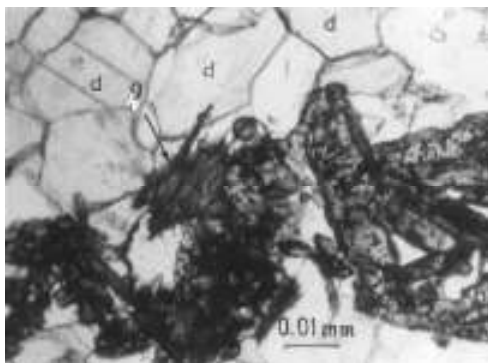


Fig. 2. A veinlet of hancockite (h) and Sb-bearing gahnite (g) enclosed in dolomitic marble (d). N //

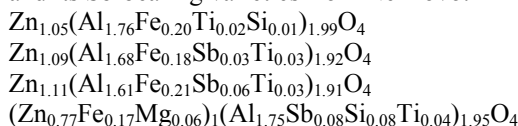
Фиг. 2. Прожилка от ханкоцит (h) и Sb-съдържащ гаанит (g), включени в доломитизиран мрамор (d). N //

Gahnite and Sb-bearing gahnite

In the investigated region there are many occurrences of gahnite of nearly stoichiometric composition, enclosed in barite schists and dolomitic marbles, and characterized with regular, idiomorphic, or distorted octahedrons.

The examined Sb-bearing gahnite findings are presented with aggregations of fine-grained (from 0.002 mm up to 0.05-0.1 mm.) octahedrons or irregular tailed - fanlike elongated formations (Figs. 1, 2 and 3), with pale yellowish-greenish, on places brownish colour. These crystals are isotropic and have very high relief ($n = 1.8$).

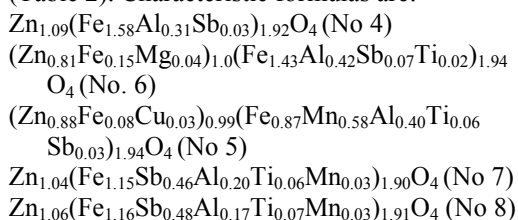
The preliminary determination of Sb-bearing gahnite composition was performed with microprobe analyses at the first opportunity by S. Korikowsky (Jančev, 1994). Further microprobe determinations are given in Table 1. The following formula characterize gahnite and its Sb-bearing varieties from Nežilovo:



Sb-bearing franklinite and antimonioan franklinite

Sb-bearing crystals of franklinite, up to 0.2 mm in size, were found in barite schists and dolomitic marbles as black, opaque corroded mal-formed octahedrons (Fig. 4A). Under the reflectance microscope they show grayish-white colour, high relief, slightly expressed reddish internal reflexes, typical isotropic properties and low R.

The determination of these peculiar spinels was performed by microprobe analyses (Table 2). Characteristic formulas are:



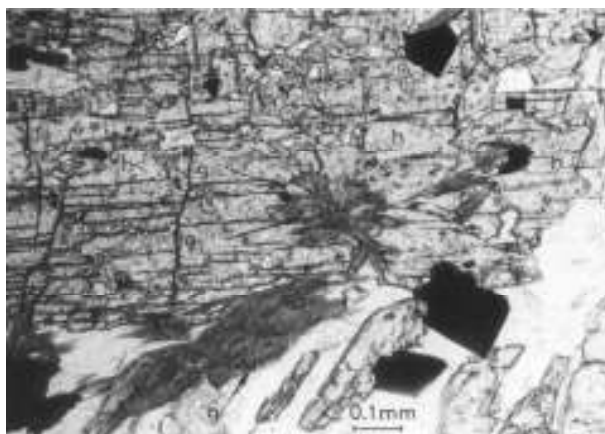


Fig. 3. Elongated and fanlike formations of Sb-bearing gahnite (g) and hematite (black) as inclusions in hancockite (h). N //

Фиг. 3. Удължени и ветрилоподобни образувания от Sb-съдържащ гаанит (g) и хематит (черно), като включения в ханкоцит (h). N //

Table 1. Representative electron microprobe analyses of gahnite (No. 1-2) and antimony-bearing gahnite (No. 3-7), wt.%

Таблица 1. Представителни микроанализи на гаанит (No. 1-2) и антимонов-съдържащ гаанит (No. 3-7), тегл.%

	1	2	3	4	5	6	7
SiO ₂	0.25	0.50	-	-	-	-	2.70
TiO ₂	0.10	-	2.78	1.40	0.62	40.68	1.82
Al ₂ O ₃	46.99	46.57	47.24	43.50	44.30	4.57	48.12
Sb ₂ O ₃	-	-	1.74	2.00	2.17	8.20	6.04
Fe ₂ O ₃	8.40	6.57	8.33	7.38	3.08	0.14	-
Mn ₂ O ₃	-	-	-	0.28	0.36	-	-
FeO	-	-	-	-	-	-	6.60
MnO	-	-	-	-	-	-	0.09
CaO	-	-	-	-	-	-	0.06
MgO	-	-	-	-	-	-	1.29
PbO	-	-	-	-	-	-	0.59
ZnO	44.72	45.48	39.57	45.19	47.04	45.16	33.60
Total	100.46	99.12	99.66	99.75	97.57	99.94	100.91
O = 4							
Si	0.01	0.02	-	-	-	-	0.08
Ti	0.02	-	0.07	0.03	0.02	0.03	0.04
Al	1.76	1.77	1.75	1.68	1.75	1.61	1.75
Sb	-	-	0.02	0.03	0.03	0.06	0.08
Fe	0.20	0.16	0.20	0.18	0.08	0.21	0.17
Mn	-	-	-	0.007	0.009	0.004	0.002
Ca	-	-	-	-	-	-	0.002
Mg	-	-	-	-	-	-	0.06
Pb	-	-	-	-	-	-	0.005
Zn	1.05	1.08	0.92	1.09	1.17	1.11	0.77

Fe and Mn contents are expressed as FeO, Fe₂O₃ or MnO, Mn₂O₃ respectively

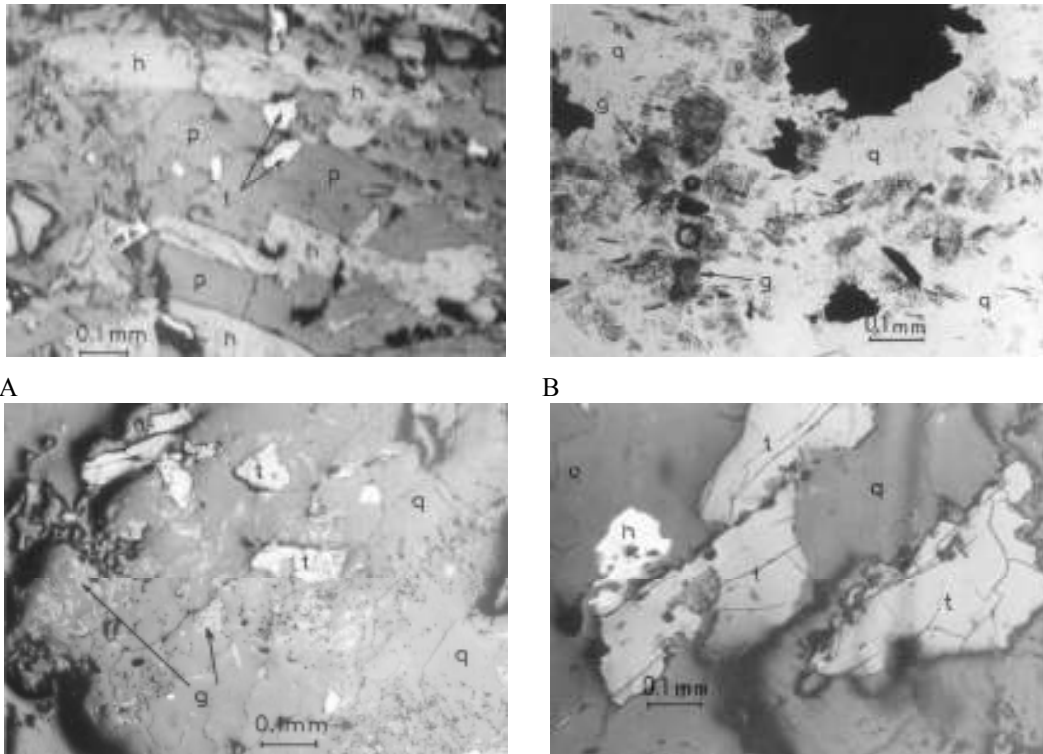


Fig. 4. Sb-bearing and antimonioanfranklinites. A. Sb-bearing franklinite (f) associated with hancockite (h) and piemontite (p) in dolomitic marble. Reflected light, N //; B. Inclusions of antimonioan franklinite (black) and Sb-bearing gahnite (g), corroded by hydrothermal quartz (q). N //; C. Inclusions of antimonioan franklinite (t) and Sb-bearing gahnite (g), corroded by hydrothermal quartz (q). Reflected light, N //; D. Inclusions of antimonioan franklinite (t) and hematite (h), corroded by hydrothermal quartz (q). Reflected light, N //

Фиг. 4. Sb-съдържащи и антимонови франклинити. А. Sb-съдържащ франклинит (f), асоцииращ с ханкоцит (h) и пиемонтит (p) в доломитизиран мрамор. Отражена светлина, N //; В. Включения от антимонов франклинит (черно) и Sb-съдържащ гаанит (g), кородирани от хидротермален кварц (q). Проходяща светлина. N //; С. Включения от антимонов франклинит (t) и Sb-съдържащ гаанит (g), кородирани от хидротермален кварц (q). Отражена светлина, N //; D. Включения от антимонов франклинит (t) и хематит (h), кородирани от хидротермален кварц (q). Отражена светлина, N //

According to the analytical data, it is obvious that examined samples are concerned with the Sb-rich franklinite group and could be concluded as follows:

- First two examined samples (No. 4 and 6), represent typical Sb-bearing franklinite.
- Analyzed sample No. 5 represents actually Mn- and Sb-bearing franklinite-hetaerolite.
- The last analyzed samples (No.7-9) are extremely Sb-enriched antimonioan franklinite

which could be a new mineral species.

This antimonioan franklinite is represented by black tabular crystals (resembling hematite), up to 0.1-0.2 mm in size. They are corroded by the younger quartz and barite (Fig. 4).

Conclusions

Continuing some earlier examinations (Jančev, 1994), in a variageted "mixed" series of the

Table 2. Representative electron microprobe analyses of antimony-bearing franklinite (No. 1-6) and antimonioan franklinite (No. 7-9), wt.%

Таблица 2. Представителни микроанализи на антимонсъдържащ франклинит (No. 1-6) и антимоноан франклинит (No. 7-9), тегл.%

	1	2	3	4	5	6	7	8	9
TiO ₂	0.61	-	0.59	-	2.29	0.55	1.93	1.95	2.52
Al ₂ O ₃	6.47	7.26	5.34	6.66	9.13	9.22	3.78	3.20	-
Sb ₂ O ₃	1.22	1.98	1.67	1.95	1.94	4.62	25.26	25.72	36.84
Mn ₂ O ₃	0.22	-	0.91	-	20.39	-	0.90	0.88	-
Fe ₂ O ₃	54.08	53.47	54.69	52.94	33.73	53.67	34.29	34.25	37.03
MgO	-	-	-	-	-	0.63	-	-	-
ZnO	37.32	35.71	36.42	37.31	31.77	28.18	31.61	32.00	23.34
CuO	-	0.88	-	1.07	0.55	-	1.83	1.58	-
Total	99.92	99.30	99.62	99.93	99.80	96.87	99.60	99.58	99.73
O = 4									
Ti	0.02	-	0.02	-	0.06	0.02	0.06	0.07	0.09
Al	0.30	0.36	0.25	0.31	0.40	0.42	0.20	0.17	-
Sb	0.02	0.03	0.03	0.03	0.03	0.07	0.46	0.48	0.71
Mn	0.01	-	0.03	-	0.58	-	0.03	0.03	-
Fe	1.60	1.57	1.63	1.58	0.95	1.58	1.15	1.16	1.10
Mg	-	-	-	-	-	0.04	-	-	-
Zn	1.08	1.03	1.06	1.09	0.88	0.81	1.04	1.06	0.81
Cu	-	0.03	-	0.03	0.03	-	0.06	0.05	-

metamorphic complex of the Pelagonian massif near Nežilovo village in Macedonia, in addition to the normal gahnite, some new peculiar Sb-bearing members of the gahnite-franklinite group of the spinels were discovered. The new found varieties are: Sb-bearing gahnite with 1.74-6.04 wt.% Sb₂O₃ and Sb-bearing franklinite with 1.22-4.62 wt.% Sb₂O₃. An Sb-bearing franklinite-hetaerolite with 1.94 wt.% Sb₂O₃, contains also 20.39 wt.% Mn₂O₃. Especially interesting is an extremely Sb-rich member, an antimonioan franklinite containing up to 25.26-36.84 wt.% Sb₂O₃, which seems to be a new mineral species inside the spinel group of minerals.

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