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Manganoan amphiboles from the skarn-ore Pb-Zn deposits in the Madan district, Central Rhodopes, Bulgaria

Rossitza D. Vassileva, Ivan K. Bonev

Abstract. Manganoan amphiboles from the skarn-ore Pb-Zn deposits in Central Rhodopes occur generally as fine fibrous aggregates. According to their chemical features manganoan amphiboles belong to two main groups: 1. calcic amphiboles – mangano-ferro-actinolite, and 2. subcalcic Mg-Fe-Mn-Li amphiboles – members of manganocummingtonite-manganogrunerite series. These minerals are formed during the hydrothermal alteration of skarn clinopyroxenes – by topotaxic replacement of manganoan hedenbergite in the first case, and replacement of johannsenite in the second case. Main chemical characteristic is their increased manganoan content, inherited from the prime pyroxenes, reaching 10.48 wt.% MnO in mangano-ferro-actinolite and up to 13.58 and 13.89 wt.% MnO in manganocummingtonite and manganogrunerite, respectively. Manganoan amphiboles are the earliest alteration products after skarn pyroxenes. They could be observed as inclusions in the later-formed phases: rhodonite, quartz, carbonate minerals and sulphides. Mangano-ferro-actinolite, manganocummingtonite and manganogrunerite are observed for the first time in Bulgarian mineral deposits.

Key words: mangano-ferro-actinolite, manganocummingtonite, manganogrunerite, skarn Pb-Zn deposits, Central Rhodopes

Address: Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; E-mail: rosivas@geology.bas.bg

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Резюме. Мангановите амфиболи от скарново-рудните оловно-цинкови находища в Централните Родопи се срещат основно като финовлакнести агрегати. Според химизма си те се отнасят към две основни групи: 1. към калциевите амфиболи – мангано-фероактинолит и 2. към субкалциевите Mg-Fe-Mn-Li-еви амфиболи - членове от редицата манганокъмингтонит-манганогрунерит. Образувани са при хидротермалната промяна на скарнови клинопироксени - чрез топотаксично заместване на манганов хеденбергит в първия случай, и на йохансенит - във втория. Характерното за тези минерали повишено манганово съдържание е унаследено от пироксените и достига до 10,48 тегл.% при мангано-фероактинолита и до 13,58 и 13,89 тегл.%, съответно при манганокъмингтонита и манганогрунерита. Мангановите амфиболи са най-ранни променителни продукти на скарновите пироксени и се срещат като включения в останалите, по-късно образувани фази: родонит, кварц, калцит и сулфиди. Това са първите доказани находки на високоманганови амфиболи в български минерални находища.

Ключови думи: мангано-фероактинолит, манганокъмингтонит, манганогрунерит, скарнови оловно-цинкови находища, Централни Родопи

Адрес: Геологически институт, Българска академия на науките, София 1113

Introduction

Manganoan amphiboles are rather rare minerals. According to the nomenclature of amphiboles, recently accepted by the Sub-commitee on Amphiboles of the International Mineralogical Association (IMA) (Leake et al., 1997) they mostly belong to two important mineral groups: calcic amphiboles and Mg-Fe-Mn-Li amphiboles. Among the calcic group these are the manganoan varieties of the tremolite-ferro-actinolite series, for instance, manganoan actinolite. In the group of the subcalcic Mg-Fe-Mn-Li amphiboles important are two manganoan species, mangano-cummingtonite (Mn-Mg amphibole) and manganogrunerite (Mn-Fe amphibole). In the mineralogical literature, including in the New Dana's Mineralogy (Gaines et al., 1997), for the last two minerals the names tirodite and dannemorite were widely used. However, now it is recommended (Leake et al., 1997) these names to be abandoned.

Manganoan amphiboles commonly occur in two types of geological environment: in metamorphic mangan-bearing rocks, and in mangan-bearing skarns. Mn-enriched silicate-carbonate and oxide rocks, metamorphosed in the conditions of the amphibolite facies (T 600-700^{o}C and pressure of several kbar) usually contain Mn-Mg amphiboles with moderate to low manganoan content. Deposits of these rocks are known from India (Dasgupta et al., 1988), Japan (Aikawa et al., 1979), Ghana, Brazil, USA and others. They are associated with garnets, pyroxenoids, rhodochrosite, etc.

Manganoan amphiboles related to skarn-polymetallic deposits are known from some Far East deposits (Kazachenko et al., 1981): manganoan actinolite with 8.43 wt.% MnO (in fact, ferro-actinolite with Fe/Mg>1) and dannemorite with 15.89 wt.% MnO (predominantly, manganogrunerite with Fe/Mg>1). Similar are the Mn-rich calcic amphiboles of tremolite-ferro-actinolite series, described from skarn deposits in the Bergslagen district, Central Sweden (Damman, Lustenhouwer, 1992), where the type deposit of dannemorite - Dannemora is also located. Manganoan content in these actinolites reaches the maximum values reported for these minerals - 19.46 wt.%.

The crystal structure, Fe-Mg ordering and the P21/m-C2/m transition in the cummingtonite-grunerite series are studied by Hirschmann et al. (1994) and Yang and Hirschmann (1995). The ordering of Mn and Mg in the cummingtonite structure especially in the manganoan members of this group was studies by applying high-temperature neutron powder diffraction (Reece et al., 2000). It was found out that Mn occupies the M(4) and M(2) sites with priority to the larger and more distorted M(4) site. At high temperature the ordering is reduced.

For first time fine fibrous mangan-bearing amphiboles from Bulgaria were described by Bonev (1968), as alteration product after skarn pyroxenes from the Madan Pb-Zn deposits. Their determination as calcic amphiboles of tremolitic type was based on optical and powder X-ray data. Lately, Bonev (1991) pointed out the existence of fibrous amphibole, replacing hedenbergite in the skarn deposit of Ardino. On the base of chemical composition and X-ray diffraction data this mineral was determined as manganoactinolite with 1.90-5.09 wt.% MnO and 11.30-12.30 wt.% CaO. In accordance with the recently approved nomenclature (Leake et al., 1997), this mineral should be denoted as manganoan ferro-actinolite.

During the systematic studies of the skarn mineralization in the Madan deposits (Ossikovo, Mogilata, Zapadno Gradishte) it was established that amphiboles are widely distributed, although in small quantities. It was found the existence of subcalcic amphiboles from the manganocummigtonite-mangano-grunerite series, as well as calcic mangano-ferro-actinolite. The results of their mineralogical study, given in the present work are important for understanding the processes of hydrothermal alteration of the early pyroxene skarns and of ore deposition in these deposits. The high manganoan content of these amphiboles is one of the manifestations of the regional geochemical manganoan specialization of the Central Rhodopes region.

Geological environment

The Tertiary, Pb-Zn vein and metasomatic ore deposits from the Central Rhodopes are hosted preferentially in the Rhodopian metamorphic complex, consisted of various gneisses, amphibolites and marbles. The ore controlling fault system is of NNW orientation (Kolkovski et al., 1996). The metasomatic skarn-ore bodies are embedded in the three known main marble horizons along the steep ore-conducting faults and have variable morphology, including bed-like, mushroom-like, vein-like and irregular shapes. Primary skarns consist of radiating clinopyroxene aggregates, varying in composition from manganoan hedenbergite to pure johannsenite. Manganoan pyroxenes have undergone intensive hydrothermal alteration and were replaced by retrograde silicate and carbonate minerals also enriched in manganese, represented by manganoan amphiboles, rhodonite, pyroxmangite, bustamite, manganoan ilvaite, rhodochrosite, manganoan calcite, manganoan chlorites and others. Clinopyroxene skarns are favourable environment for localization of the rich metasomatic galena-sphalerite-quartz ores. Sulphide deposition is closely connected with the processes of retrograde skarn alteration and especially of the widely-distributed carbonatization.

Methods and materials

Mineral relationships and paragenetic sequences of amphiboles and the other minerals were determined by macroscopic observations, and in the microscopic studies using polarising microscope in transmitted and reflected light. Fine-fibrous amphiboles are often included in a carbonate mass, whose selective dissolution gives opportunity to extract the individual fibres and fibrous aggregates thus making them accessible for direct observation. Morphology of these peculiar fibrous formations and their orientation with respect to primary pyroxene was studied by applying SEM on carbon-coated samples. Chemical analyses were performed by using an electronprobe microanalyser JEOL Superprobe 733 equipped with an ORTEC EDS system, at 15kV and 1nA. The following standards were used: albite for Na, diopside for Mg, Fe_2O_3 for Fe, Ai_2O_3 for Al, SiO_2 for Si, K-feldspar for K, apatite for Ca, TiO_2 for Ti, manganoan ilmenite for Mn. Mineral diagnostics was proved by X-ray methods with a Gandolfi camera and photographic registration. Representative sample of studied material is deposited at the collections of the Geological Institute under № M1.2001.3.

Mangano-ferro-actinolite

Mangano-ferro-actinolite was found in skarn-ore samples from the Ossikovo and the Zapadno Gradishte deposits. This mineral is developed after manganoan hedenbergite (Fig. 1).

Physical properties. Mangano-ferro-actinolite from the studied deposits is presented by pale

Fig. 1. SEM microphotograph of manganoan hedenbergite (Px) replaced by fibrous mangano-ferro-actinolite (Act). Zapadno Gradishte

Фиг. 1. СЕМ изображение на манганов хеденбергит (Px), заместен от мангано-фероактинолит (Act). ЗападноГрадище

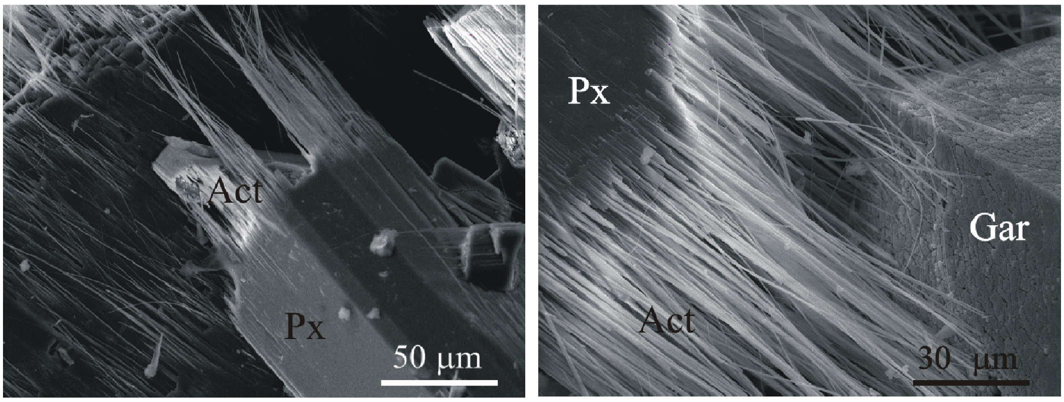

Fig. 2. Topotaxic replacement of manganoan hedenbergite (Px) from mangano-ferro-actinolite (Act). Gar – garnet. Zapadno Gradishte
Фиг. 2. Топотаксично заместване на манганов хеденбергит (Px) от мангано-фероактинолит (Act). Gar – гранат. Западно Градище

green to snow-white fine-fibrous crystals (Fig. 2), which are 1-1.5 mm in length and below 1 µm wide. Usually they occur as parallel aggregates with silky luster, inheriting the texture of the prime skarn pyroxene (Fig. 3). They are colorless and transparent, non-pleochroic, with extinction angle Z^*c* of 10°. Elongation, as in all fibrous amphibole varieties (Gaines et al., 1997) is positive.

Chemical composition and crystal chemistry. Chemical composition of the studied amphiboles is quoted in Table 1, and presented on Fig. 4 as well. The components in the general chemical formula of amphibole $AB_2C_5T_8O_{22}(OH)_2$ could be grouped as follows: A – K, Na; B – Ca, Na, Mn; C – Mn, Fe, Mg, Ti; T – Si, Al, Ti (Leake et al., 1997). The group of calcic amphiboles with ferro-actinolite composition is defined as monoclinic members in which $Ca_B>1.5$, $Ca_A<0.5$, $(Na+K)_A<0.5$, and $Mg/(Mg+Fe)<0.5$. In this case manganoan content can be rather high.

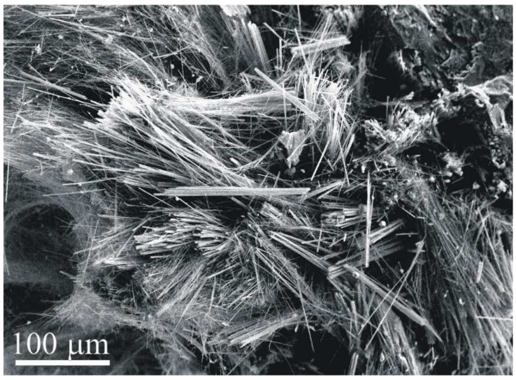

Fig. 3. Fine-fibrous aggregates of mangano-ferro-actinolite. Ossikovo
Фиг. 3. Финовлакнести агрегати на мангано-фероактинолит. Осиково

The site occupancy was calculated using the method proposed by Leake et al. (1997). The ratio Mg/(Mg+Fe) in all analyses is around 0.4, and Ca in the range 1.53-1.56 apfu. MnO content varies in the range 7.86-10.48 wt.% and the atomic proportion of Mn, ranging from 1.11 to 1.38 apfu, is always in the limits of $1<Mn<2.99$, which defines the studied calcic amphibole as mangano-ferro-actinolite. Al^{3+} has low content reaching 0.4 apfu and together with Ti^{4+} (up to 0.01 apfu) and Si^{4+} fulfills the tetrahedral (T) sites to 8. The octahedral C position, which includes M1, 2M2 and 2M3 sites, is occupied by five atoms of Fe^{2+}, Mg^{2+} and Mn^{2+} (0.7-0.75 apfu). Calcium enters preferentially the larger octahedral B (M4) position with content of 1.65 apfu, together with a part of Mn^{2+} atoms (from 0.38 to 0.68 apfu). The content of Na and K in the A-position does not exceed the value of 0.22 apfu.

Table 1. *Representative electron microprobe analyses of clinopyroxenes and manganoan amphiboles replacing them*

Таблица 1. *Представителни микросондови анализи на клинопироксени и заместващите ги манганови амфиболи*

Deposit	Zapadno Gradishte	Mogilata	Zapadno Gradishte		Mogilata			
Mineral	Manganoan hedenbergite	Johannsenite	Mangano-ferro-actinolite		Mangano-cummingtonite		Mangano-grunerite	
Analysis N	1	2	3	4	5	6	7	8
SiO_2	48.21	46.78	49.00	48.79	54.34	52.90	52.50	52.40
TiO_2	0.11	0.00	0.02	0.05	0.00	0.00	0.00	0.00
Al_2O_3	0.00	2.23	1.86	2.11	0.00	1.32	0.71	0.22
FeO	15.98	4.91	20.10	20.65	15.99	16.11	19.54	19.95
MnO	11.57	23.48	10.48	9.50	13.34	13.58	13.63	13.89
MgO	2.30	1.43	7.35	6.78	14.20	12.98	9.77	9.88
CaO	20.65	21.68	9.23	9.87	0.77	0.87	1.74	1.20
Na_2O	0.18	0.26	0.58	0.26	0.28	0.59	0.46	0.43
K_2O	0.36	0.00	0.20	0.19	0.06	0.00	0.20	0.18
Total	99.36	100.77	98.82	98.20	98.98	98.35	98.55	98.15
Cations	O = 6		O = 23					
Si	1.99	1.91	7.59	7.60	8.03	7.90	7.99	8.03
Al	0.00	0.11	0.34	0.39	0.00	0.10	0.11	0.00
Ti	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
T-site			7.93	7.99	8.03	8.00	8.00	8.03
Al			0.00	0.00	0.00	0.14	0.02	0.04
Mg	0.14	0.09	1.70	1.57	3.13	2.98	2.22	2.26
Fe^{2+}	0.55	0.17	2.60	2.69	1.98	2.01	2.49	2.56
Mn	0.40	0.81	0.70	0.74	0.00	0.00	0.28	0.15
C-site			5.00	5.00	5.00	5.00	5.00	5.00
Fe^{2+}			0.00	0.00	0.00	0.00	0.00	0.00
Mn			0.68	0.51	1.67	1.72	1.48	1.65
Mg			0.00	0.00	0.00	0.00	0.00	0.00
Ca			1.53	1.65	0.12	0.14	0.28	0.20
Na			0.00	0.00	0,08	0.00	0.14	0.13
B-site			2.21	2.16	1.97	1.99	1.90	1.98
Total			15.14	15.15	15.00	14.99	14.90	15.01
Na	0.01	0.02	0.17	0.08	0.00	0.17	0.00	0.00
K	0.02	0.00	0.04	0.04	0.11	0.00	0.04	0.04
A-site			0.21	0.12	0.11	0.17	0.04	0.04
Mg/(Mg+Fe)			0.40	0.37	0.61	0.59	0.47	0.47

During a systematic study of mangan-rich calcic amphiboles from the tremolite-ferro-actinolite series in some Swedish skarn deposits, Damman and Lustenhouwer (1992) pointed out the existence of a miscibility gap in the area of the ferroan members. Our analyses of mangano-ferro-actinolites are plotted exactly in the middle of this area (Fig. 4), witnessing to the absence of such miscibility gap. In the full solid-solution series of Fe and Mn actinolites, the studied here samples represent ferro-actinolites with the highest known manganoan content.

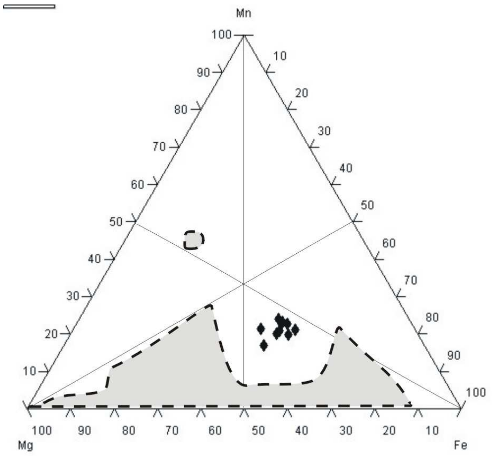

Fig. 4. Cations composition in the M1-M3 sites of mangano-ferro-actinolite from the Madan district (rhombs). Grey fields represent distribution of Mg, Fe and Mn in tremolite-ferro-actinolite amphiboles from Sweden, after Damman and Lustenhouwer, 1992

Фиг. 4. Катионен състав в М1-М3 позициите на мангано-фероактинолит от Маданския район (ромбове). Полетата очертават разпределението на Mg, Fe и Mn в тремолит-фероактинолитовите амфиболи от Швеция, по Damman & Lustenhouwer, 1992

Manganocummintonite and mangano-grunerite

High-manganoan subcalcic amphiboles determined from the Mogilata deposit are developed by partial replacement of ferroan johannsenite. They are associated with rhodonite, quartz, and often, with an extremely mangan-rich ilvaite (Vassileva et al., 2001).

Physical properties. These amphiboles are presented by white and pale beige fibres and whiskers. Their length is relatively shorter than those of the calcic amphiboles reaching 1 mm, the width is around 10-12 µm. Sometimes they form characteristic fibrous aggregates with rounded voids (Fig. 5), imprints of leached calcite crystals. Extinction angle Z^*c* measured is 18°. Pleochroism was not observed.

Chemical composition and crystal chemistry. The group is defined as possessing $(Ca+Na)_B<1$ and $(Mg+Mn+Fe)>1$ in the standard amphibole formula. In cases when $1<Mn<2.9$, the Mg/(Mg+Fe) ratio 0.5 (i.e. "the 50% rule") determines (Leake et al., 1997) the dividing line between the magnesian and iron members, manganocummingtonite and manganogrunerite, respectively. In the analyzed by us amphiboles, manganoan content reaches 13.58 wt.% in manganocummingtonite and 13.89 wt.% in manganogrunerite (Tabl. 1, Fig. 6). The ratio Mg/(Mg+Fe) is larger than 0.5 in most of the analytical points and varies in the range 0.55-0.72 for manganocummingtonite. When this ratio is <0.5 (mean 0.47) the studied mineral should be considered as manganogrunerite.

The sum (Mg+Mn+Fe) is always >1, ranging in the narrow limits of 6.2-6.6 apfu. Mn^{2+} content varies from 1.2 to 1.7 apfu, and combined with Fe and Mg, occupies the octahedral C (M1, M2 and M3) positions. Tetrahedral T-positions are nearly almost filled by the atoms of Si^{4+}, which distinguish the studied subcalcic amphiboles from calcic mangano-ferro-actinolite. 80% of the A-position remains unoccupied, whereas Mn enters the M4, together with small amount of Ca. The compositions of the manganocummingtonites plotted on the Mg-Fe-Mn+Ca diagram are closely to the Fe = Mn(+Ca) line.

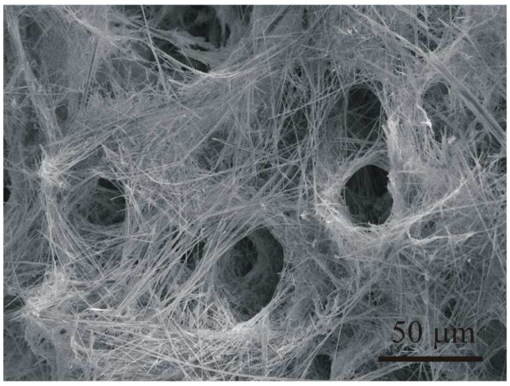

Fig. 5. Manganocummingtonite aggregate with rounded voids formed by dissolution of calcite

Фиг. 5. Порест агрегат от манганокъмингтонит с празнини, формирани при разтваряне на калцит

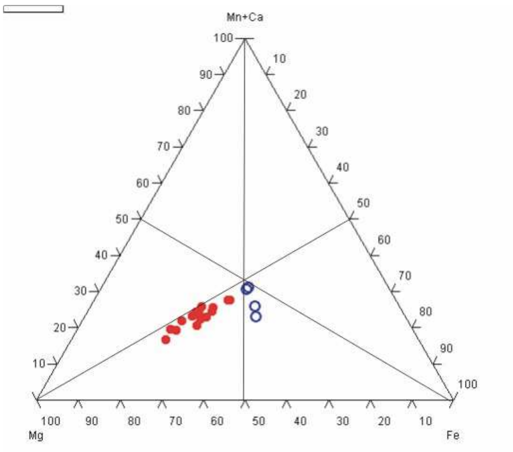

Fig. 6. Cations composition of manganocummingtonite (circles) and manganogrunerite (empty circles) from the Madan district

Фиг. 6. Катионен състав на манганокъмингтонит (кръгчета) и манганогрунерит (празни кръгчета) от Маданския район

Mineral relationships

Mangano-ferro-actinolite from the Zapadno Gradishte and Ossikovo deposits was always formed by topotaxic replacement of *manganoan hedenbergite* with parallel *c*-axes. SEM observations show that the fine fibrous amphiboles inherit the direction of the structural chains on *c* direction of the initial clinopyroxene (Fig. 7). Interstitial voids between pyroxene relics and amphibole fibres are filled by manganoan calcite.

The replacement of low-ferroan *johannsenite* leads to formation of amphiboles of manganocummingtonite-manganogrunerite series, which overgrow and often fully replace the manganoan pyroxene. These amphiboles are typical with their fibrous aggregates with rounded voids, formed by dissolved calcite (Fig. 5).

Minerals from manganocummingtonite-manganogrunerite series from the Ossikovo and Mogilata deposits are often found associated with *rhodonite*. Microscopic and SEM observations lead to the conclusion that formation of these amphiboles preceeds that of rhodonite. In samples from Zapadno Gradishte rhodonite, which is widely distributed though in subordinate quantities, often contains inclusions of fine-fibrous mangano-ferro-actinolite parallel to the prime pyroxene elongation. Rhodonite crystals and aggregates have not the same orientation. In samples from Ossikovo and Mogilata, rhodonite

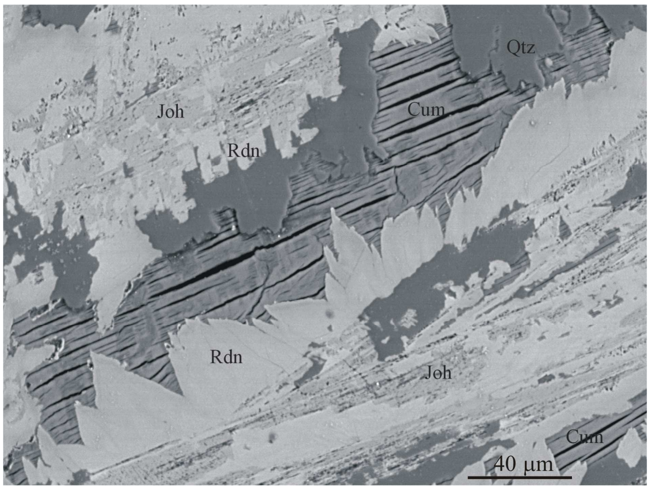

Fig. 7. Replacement of johannsenite (Joh) from manganocummingtonite (Cum) with quartz (Qtz) and subsequently formed rhodonite (Rdn) euchedral crystals

Фиг. 7. Заместване на йохансенит (Joh) от манганокъмингтонит (Cum) с кварц (Qtz) и по-късни родонитови (Rdn) идиоморфни кристали euhedral crystals are formed after pyroxene and often crosscut the mangano-cummingtonite layers (Fig. 7). Other retrograde products and sulphide ores are overimposed on this early paragenesis.

Manganoan ilvaite, which is formed together with or shortly after the main ore sulphides, forms single crystals and nests at the skarn front or in the manganoan hedenbergite zone (Vassileva et al., 2001). Sphalerite and quartz are also presented in these nests, the central parts of which are filled by calcite. The ilvaite grains often include fine fibres of mangano-ferro-actinolite in random orientation. Sometimes, when the nests are in a rhodonite mass, relics of manganocummingtonite and manganogrunerite are observed as inclusions in this mineral. These amphiboles inherit the radial texture and orientation of the prime johannsenite. Fibrous inclusions of mangano-ferro-actinolite are also typical for the *andraditic garnet* in the deposit of Zapadno Gradishte, which is formed as a late hydrothermal product after the hedenbergite skarns.

Microscopic observations of transparent *sphalerite* crystals sometimes also revealed the presence of amphibole fibres. The fine fibrous inclusions in galena shown on an electron microscopic microphotograph by Bonev (1980, Tabl. XII, Fig. 1b) are also, most likely, of such amphiboles.

Carbonatization is a widespread hydrothermal alteration of skarns. *Carbonate* minerals often contain inclusions of actinolitic amphiboles. Manganoan calcite and rhodochrosite fill the interstices between the primary skarn and postskarn minerals, as well as the nests in the pyroxene mass. Typical for the metasomatic bodies of Mogilata and Ossikovo is the presence of fine-prismatic *green quartz*. Its color is caused by the fine fibrous inclusions of mangano-ferro-actinolite.

The process of metasomatic replacement of manganoan hedenbergite by mangan-ferro-actinolite may be presented by the following reaction:

$$5Ca(Fe,Mn,Mg)Si_2O_6 + 3CO_2 + H_2O =$$

manganoan hedenbergite

$$Ca_2(Fe, Mg, Mn)_5Si_8O_{22}(OH)_2 + 3CaCO_3 + 2SiO_2$$

mangano-ferro-actinolite calcite quartz

The reaction leads to extraction of Ca and Si from the pyroxene and to reduction of the volume of the new-formed silicate – mangano-ferro-actinolite. Calcium fixed as carbonates and Si fixed in quatrz filled the opened free space around the new-formed minerals. In the case, when after johannsenite are formed subcalcic amphiboles from manganocummingtonite-manganogrunerite series together with rhodonite, Ca is almost fully extracted and the needed Fe and Mn are probably taken from the close environment.

Conclusions

1. Microscopic observations of the mineral relationships in the skarn lead-zinc deposits of the Madan district prove that manganoan amphiboles are the earliest products of retrograde alteration of the primary pyroxene skarns.
2. The chemical composition of the amphiboles is closely related to the chemistry and the Fe-Mg-Mn ratio of the two chemical types of replaced pyroxenes. The calcic amphiboles (mangano-ferro-actinolite) are formed after manganoan hedenbergite, whereas the amphiboles of subcalcic (manganocummingtonite-manganogrunerite) series replace johannsenite. Some other amphibole compositions are also possible.
3. Pyroxene to amphibole transition is controlled by the structural similarities of these chain silicates. It is connected with extraction of Ca from the pyroxene structure and it's deposition as manganoan carbonates in the close vicinity.
4. The new obtained chemical data, confirm the existence of full solid-solution series between manganocummingtonite and manganogrunerite, without the miscibility gap, suggested earlier (Damman, Lustenhouwer, 1992). In Ossikovo and Mogilata manganocummingtonite prevails over manganogrunerite.
5. Mangano-ferro-actinolite, manganocummingtonite and manganogrunerite are observed for the first time in Bulgarian mineral deposits.

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