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Rare-earth and some trace elements in the metasomatic skarn-ore bodies of the Madan Pb-Zn deposits, Bulgaria

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Abstract. A systematic study on distribution of rare-earth and some other trace elements in the mesothermal skarn Pb-Zn deposits from the major Madan ore district, in the Central Rhodopes, Bulgaria, was performed. The metasomatic skarn-ore bodies are enclosed in the marble horizons of the high-grade Rhodope gneissic metamorphic complex along large NNW ore-controlling and ore-bearing faults. Three representative deposits were investigated: Ossikovo and Zapadno Gradishte, located in the western slope of the Madan dome structure (Madan allochthone), and Enyovche, in the eastern slope (Startsevo allochthone). The marbles have been successively replaced by skarn clinopyroxenes of the hedenbergite-johannsenite series, followed by rhodonite, and the main sulphide mineralisation (galena, sphalerite, pyrite) with quartz, and in some deposits also by bustamite, manganoan andradite, manganilvaite, carbonate and some other minerals.

The marbles show very low *REE* content in the western slope (*ΣREE* 0.87-2.10 ppm) and some higher in the eastern slope (Enyovche) (*ΣREE* 26.8 ppm) with clear enrichment of *LREE* over *HREE* at the chondrite-normalised *REE* patterns. It is suggested that the decreasing content of *REE* from La to Lu is determined by the gradually increasing of their radius difference with Ca, which octahedral positions are the only suitable sites for incorporation of *REE* in the calcite structure. At the low *REE* mobility in hydrothermal conditions the skarn pyroxenes and replacing them retrograde silicate minerals inherited the general character of the *REE* patterns of marbles. Slight successive enrichment in the later minerals was observed following the order of their deposition. In rhodonite, the richest in Mn mineral, some enrichment of Lu is fixed in most analyses, related to the similarities in the ionic radii of Mn and Lu. The trace elements of chalcophyllic character (Ga, Ge, Mo, Sn) are related to sulphides formed in the hydrothermal process.

Key words: *REE*, trace elements, marbles, skarns, Madan Pb-Zn deposits

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Резюме. Проведено е систематично изследване на разпределението на редкоземните и някои други елементи-следи в мезотермалните скарнови Pb-Zn находища от Маданския руден район. Метасоматичните скарново-рудни залежи са вместени в мраморните хоризонти на Родопския метаморфен комплекс около големи ССЗ рудоконтролиращи разломни структури. Три представителни находища са изследвани: Западно Градище и Осиково, вместени във втория и третия мраморни хоризонти от западното крило на Маданската куполна структура (Мадански алохтон), и Еньовче - от горните мрамори в източното й крило (Старцевски алохтон). Мраморите са последователно заместени от скарнови клинопироксени от хеденбергит-йохансенитовия ред, последвани от родонит и главните рудни сулфиди (галенит, сфалерит, пирит) с кварц, наместа от бустамит, манганов андрадит, манганилваит, карбонати и някои други минерали.

Мраморите имат твърде ниско съдържание на *REE* (*ΣREE* 0.87-2.10 ppm) в западната част и малко по-високо (*ΣREE* 26.8 ppm) в източната част (Еньовче) с ясно обогатяване на леките редки земи над тежките в хондрит-нормираните модели. Вероятно, намаляващото съдържание на *REE* от La към Lu се определя от постепенното увеличаване на разликата в йонните им радиуси спрямо Ca, чийто октаедри са единствената подходяща позиция за включването им в калцитовата структура. При ограничената подвижност на тези елементи в хидротермалния процес, скарновите пироксени и заместващите ги ретроградни силикатни минерали запазват общия характер на *REE* моделите в мраморите. Отбелязва се слабо общо обогатяване при по-късните минерали, в порядък на тяхното отлагане. В родонита, най-богатия на манган силикатен минерал, известно набогатяване на Lu се установява в повечето анализи, което вероятно е свързано с близките йонни радиуси на Mn и Lu. Елементите-следи с халкофилен характер (Ga, Ge, Mo, Sn) са свързани с рудни сулфидни минерали, образувани в хидротермалния процес.

Introduction

Geochemistry of trace and rare-earth elements is rapidly developing during the last few decades and is applied to study diverse processes in the Earth's crust. It is particularly efficient in studies of magmatic processes, of plutonic, volcanic and dyke rocks and their products in diverse geodynamic environments. However, the behaviour of these elements in the hydrothermal ore-forming processes is not well known and only just recently began to attract attention. Such studies have been conducted on some of the main hydrothermal non-metallic minerals – carbonates (Bau, Möller, 1992; Davies et al., 1998), fluorite (Schneider et al., 1975; Bau et al., 2003), anhydrite (Bach et al., 2003), etc. The information about skarn-ore deposits is still insufficient. An essential difference of these deposits, as compared to the magmatic rocks, is that they originated during a relatively long hydrothermal process in which earlier skarns, becoming later non-equilibrium products, were successively replaced by a series of subsequent retrograde minerals under the influence of next portions of hydrothermal fluids.

In the course of a systematic complex study of lead-zinc deposits in the metamorphic rocks of the Central Rhodopes, we have made the first attempt to obtain similar information about the content and distribution of rare-earth and some trace elements in these hydrothermal ore mineralisations. Our attention was focused on some characteristic skarn Pb-Zn deposits in the largest ore region – the Madan district. The high manganese specialisation of the Rhodope deposits, extremely high as compared to most of the known skarn lead-zinc deposits (Einaudi et al., 1981), is of particular interest. The high Mn content in the skarns influenced in a specific manner the behaviour of rare-earth and trace elements during the hydrothermal process. The present paper reports some results of these studies. They are based on systematically collected mineralogical information about the skarns and their retrograde alteration during the ore mineralisation process.

Geological setting

The Tertiary mesothermal vein and metasomatic lead-zinc deposits in the Central Rhodopes are hosted in the high-grade metamorphic rocks of the Rhodope Massif and partially in their Paleogene sedimentary cover. The metamorphic complex consists of two parts (Kozhoukharov, 1984). The lower part, assigned (Ivanov, 2000) to the Arda unit of the Central Rhodope Metamorphic Group, is composed of migmatised gneisses that form the core of the Central Rhodope (Madan) dome (Fig. 1). The upper overthrusted part, exposed along the western and eastern margins of the dome, is referred to as Madan or Startsevo allochthone and comprises diverse gneisses, amphibolites, schists and marbles. Productive marble beds, which host the metasomatic skarn-ore mineralisation, are found in one to three horizons of the two parts of the metamorphic complex. The lower (first) marble

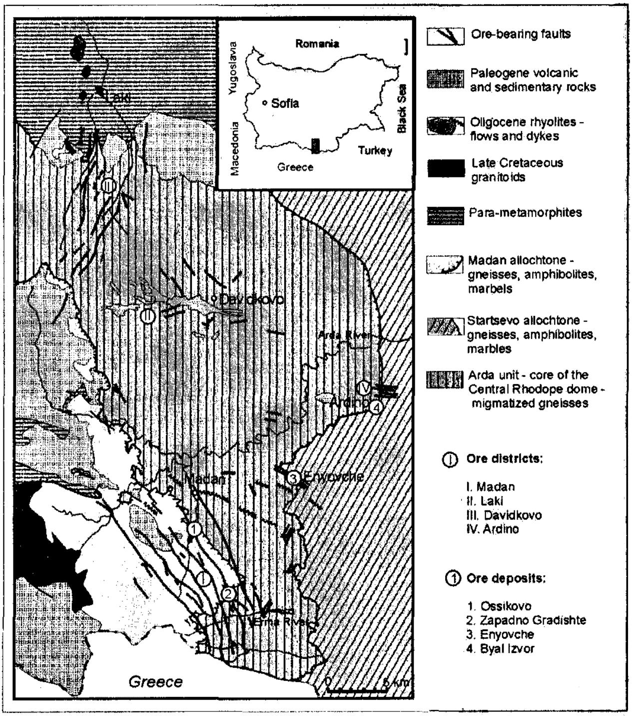


Fig. 1. Geological map of the Central Rhodopes, modified after Ivanov et al. (2000)
Фиг. 1. Геоложка карта на Централните Родопи, по Ivanov et al. (2000), с изменения

horizon, known in the southern part of the region, is a thick marble massif that is not exposed on the surface and for the time being is not well studied. The upper two (second and third) marble horizons host the major accessible metasomatic ore bodies. These two horizons are assigned to the Chepelare (Lower Variegated) Formation, which lies at the base of the allochthone directly above the thrust surface, assumed to be a detachment fault. Single rhyolite subvolcanic bodies and dykes cut the metamorphic rocks.

The hydrothermal mineralisation is represented by ore veins controlled by steeply dipping fault zones, and by metasomatic skarn-ore bodies within the marble horizons around the ore veins. Up to now no relations to any magmatic activity and rocks have been detected.

Among the four ore regions in the Central Rhodopes (Madan, Laki, Davidkovo and Ardino), the Madan district is the largest and most important from economic viewpoint (Kolkovski et al., 1996). The ore mineralisations in the district are controlled by six large (up to 10-15 km long) and some smaller NNW trending fault zones that host the ore veins. The metasomatic infiltration skarn-ore bodies around these zones show diverse morphology depending on the size of the mineralised veins and on the thickness of the marble beds (Bonev, 2003). The marbles of the upper two marble horizons are white, massive, fine- or medium-grained rocks, composed almost entirely of calcite, with insignificant amounts of MgO (0.3-1.8 wt. %), MnO (<0.1 wt. %), FeO (<0.2 wt. %) as pointed out earlier by

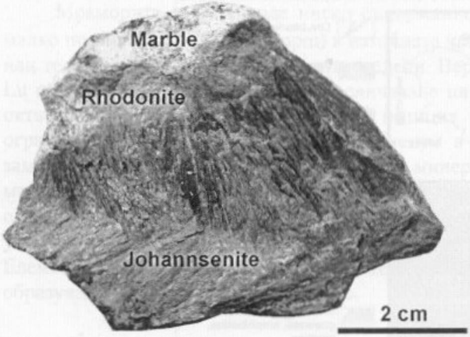


Fig. 2. Zoned skarn from the Enyovche deposit
Фиг. 2. Зонален скарн от находище Еньовче

Dimitrov (1972). Usually calcite is in equigranular crystals with perfect rhombohedral cleavage and twinning. Accessory minerals are muscovite, phlogopite, quartz. In some levels, especially in the western Madan allochthone, the marbles are graphite-bearing. No direct link of mineralisations with magmatic rocks is known.

The distal reduction skarns replacing marbles, and representing the favourable environment for the metasomatic ores, comprise manganoan clinopyroxenes (Mn-hedenbergite to johannsenite), accompanied by rhodonite and a retrograde association of pyroxenoids, manganoan amphiboles and chlorites, manganilvaite, manganoan andradite and manganoan carbonates (Vassileva, Bonev, 2003; Bonev, 2003). The most common type of primary metasomatic zoning in the skarn bodies is: fluid channel - pyroxenes – rhodonite - marble (Fig. 2). The Mn-content of the pyroxenes is high, the Mn/Fe ratio increasing toward the distal parts of the bodies and reaching maximum values around the metasomatic front with marbles where pure johannsenite often occurs. The rhodonite, forming mainly the peripheral zone of the skarn bodies, develops metasomatically and topotaxically after pyroxenes. The retrograde alterations of the skarn bodies are synchronous to the superimposed sulphide mineralisation and form a complex secondary mineral zoning. In generalised form it is as follows: ore vein – zone of massive metasomatic sulphide ore – zone of banded ores (ore rhythmites) – zone of altered (carbonatised and amphibolised) skarns with impregnated sulphide mineralisation – peripheral zone of unaltered johannsenite) skarns – rhodonite zone, sometimes with nests of manganilvaite – marbles. In some deposits, as for instance in Zapadno Gradishte (Bonev, 1978), the internal part of the pyroxene zone is replaced by bustamite, while the central zone around the vein contains also nests and disseminated crystals of late andradite accompanied by sulphides and carbonates (Fig. 3).

The present studies are focused on three representative skarn-ore deposits, which together with geological and mineralogical similarities show and specific differences in their geological setting and some mineralogical and genetic characteristics. These are the deposits in the western part of the region, in the Madan allochthone: Zapadno Gradishte and Ossikovo, related to the second and third marble horizon respectively, and Enyovche, located in the eastern part of the region, in the Startsevo allochthone (Fig. 1).

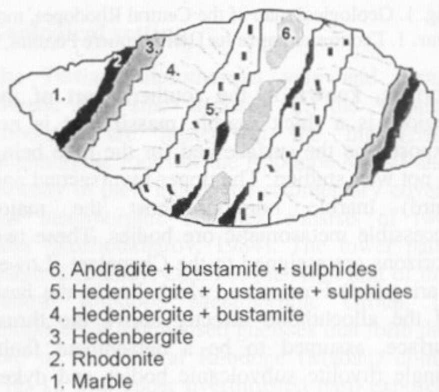


Fig. 3. Complex zoned skarn from the Zapadno Gradishte deposit. The overimposed silicate and sulphide internal zones (4-6) are developed around the central axial zone. Specimen is 21 cm long
Фиг. 3. Сложно зонален скарн от Западно Градище. Наложените силикатни и сулфидни вътрешни зони (4-6) са развити около централната осева зона. Дължината на образеца е 21 cm

Methods and materials studied

The samples studied were collected from the host marbles, from the skarn pyroxenes, rhodonite and the successive products of their later retrograde alteration: bustamite, mangan-ilvaite, andradite, carbonates and quartz. The manganoan amphiboles, which are interesting early products of pyroxene alteration (Vassileva, Bonev, 2003), occur unfortunately only in the form of fine fibres that were impossible to analyse. 20 mainly monomineral samples were studied: one specimen from Zapadno Gradishte and 2 each from the Ossikovo and Enyovche deposits. Some bulk samples were also analysed but, since the quantitative relationships between different mineral phases in the metasomatic products are strongly variable, these samples provide only general information. One sample of Mn-bearing ilvaite from the small isolated skarn-ore occurrence Byal Izvor in the eastern part of the region (Vassileva et al., 2001) was also studied for comparison. The studied samples are kept in the collections of the Geological Institute, Bulgarian Academy of Sciences (samples No M1.03.7. 1-3).

The rare-earth elements and additional trace elements were analysed by an inductively coupled plasma mass spectrometer (ICP-MS) PlasmaQuad $PQ2^+$, at the Institute of Geochemistry of the Siberian Branch of the Russian Academy of Sciences in Irkutsk. Powdered samples (0.1 g) were dissolved in Teflon pressure vessels at 220°C for 5 h and analysed with dilution factor 1000. International reference standards were used to quantify the accuracy of analyses. The analytical error was ~5% and the detection limit about 0.01 ppm.

Results

Ossikovo deposit

Marbles. The third, highest marble horizon hosting the deposit is developed in the whole region. The chondrite-normalised REE pattern of the marbles shows the following features (Table 1 and Fig. 4a):

- very low total content of rare-earth elements with *ΣREE* 2.10 ppm;
- flat *REE* pattern with *LREE* enrichment and $(La/Yb)_N$ 4.06;
- negative Eu anomaly; possibly, it is related to the reduced environment (as indicated by the local graphite enrichment of marble), when the available small calcite octahedral $^{[6]}Ca^{2+}$ sites, are unsuitable for incorporation of the much larger in ionic radius reduced Eu^{2+}.

Pyroxene, the major skarn mineral in the studied samples, is manganoan hedenbergite with composition $Ca_{0.91}Mn_{0.40}Fe_{0.55}Mg_{0.14}Si_{1.99}O_6$ (mean of 9 analyses). *Rhodonite*, formed entirely as a metasomatic product after pyroxene, has compositions $Ca_{0.20}Mn_{0.75}Fe_{0.05}Si_{0.99}O_3$ (Os8/2, from 8 analyses) and $Ca_{0.22}Mn_{0.68}Fe_{0.09}Mg_{0.01}Si_{0.98}O_3$ (Os10/1, from 9 analyses). These minerals retain both the general *REE* patterns of the initial marbles with the low total concentrations of rare-earth elements but with certain weak total *REE* enrichment (*ΣREE* 2.51 and 2.8 ppm, respectively). The Ce and Eu anomalies preserve their character. There is a slight Lu-enrichment of rhodonite Os8/2 (Fig. 4a).

Manganilvaite, $Ca_{0.92}Mg_{0.05}Fe^{2+}_{1.37}Mn_{0.72}Fe^{3+}_{0.92}Si_{2.01}O_2/O/(OH)_2$, a later retrograde post-skarn mineral, shows a similar pattern but with additional total *REE* enrichment (*ΣREE* 4.55 and 3.90 ppm). The Eu anomaly decreases and becomes even positive (Os10/2 in Fig. 4a).

Calcite, formed as the latest alteration product in the skarns, retains the generally low content of rare-earth elements (*ΣREE* 2.73 ppm). The content of the *HREE* is too low, bellow the detection limits.

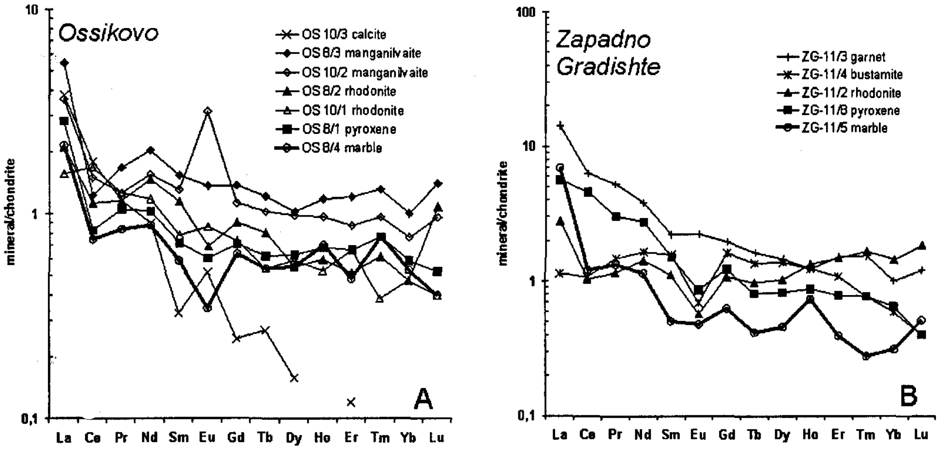
The following specific features are noted by normalising the trace element concentrations to their content in the hosting marbles (Fig. 5a): the products that replace the marbles are enriched, most probably due to contamination of the samples with dispersed remnant accessory phases (zircon – Zr and Hf) or new formed phases (probably molybdenite – Mo, barite – Ba, Rb, Cs). There is no doubt that the detected Ga and Ge are related to the mechanical admixtures of sphalerite, which

Table 1. *REE and some trace element concentrations of marbles, skarn- and post-skarn minerals from the Ossikovo deposit, ppm*

Таблица 1. *Концентрации на REE и някои елементи-следи в мрамори, скарни и апоскарнови минерали от находище Осиково, ppm*

	OS-8/4	OS-8/1	OS-8/2	OS-8/3	OS10/1	OS10/2	OS10/3
	Marble	Px	Rdn	MnIlv	Rdn	MnIlv	Ca
Sc	0.18	0.33	0.18	0.23	0.24	0.16	0.06
Co	n.d.	3.26	0.52	5.37	n.d.	6.84	n.d.
Ni	n.d.	3.77	2.18	1.91	n.d.	1.12	n.d.
Ga	0.04	2.82	6.30	4.74	1.30	4.95	0.01
Ge	0.07	1.68	1.03	7.25	1.80	7.55	0.09
Rb	0.02	0.83	0.80	0.44	0.55	0.61	0.22
Sr	135.47	84.12	10.83	4.36	8.28	4.09	134.62
Y	1.81	1.75	1.46	3.40	2.09	2.93	0.31
Zr	-	1.25	1.52	1.29	7.59	1.76	-
Nb	-	0.23	0.12	1.81	0.60	0.18	-
Mo	-	n.d.	n.d.	n.d.	3.07	n.d.	-
Sn	-	n.d.	n.d.	n.d.	0.10	n.d.	-
Cs	-	1.99	0.65	0.17	3.62	0.16	0.32
Ba	-	6.14	7.80	4.81	10.54	6.32	-
La	0.51	0.67	0.50	1.29	0.37	0.86	0.90
Ce	0.46	0.51	0.69	0.75	1.03	0.92	1.10
Pr	0.08	0.10	0.11	0.16	0.12	0.12	0.11
Nd	0.41	0.48	0.69	0.95	0.55	0.73	0.42
Sm	0.09	0.11	0.18	0.24	0.12	0.20	0.05
Eu	0.02	0.04	0.04	0.08	0.05	0.18	0.03
Gd	0.13	0.15	0.19	0.28	0.15	0.23	0.05
Tb	0.02	0.02	0.03	0.05	0.02	0.04	0.01
Dy	0.14	0.16	0.14	0.26	0.15	0.25	0.04
Ho	0.04	0.04	0.03	0.07	0.03	0.06	0.00
Er	0.08	0.11	0.09	0.20	0.11	0.15	0.02
Tm	0.02	0.02	0.02	0.03	0.01	0.03	-
Yb	0.09	0.10	0.08	0.17	0.08	0.13	-
Lu	0.01	0.01	0.03	0.04	0.01	0.02	-
Hf	-	0.03	0.04	0.04	0.20	0.04	-
Ta	-	0.13	0.01	0.19	0.06	0.05	-
W	0.00	19.57	1.13	7.26	n.d.	1.87	-
Th	0.05	0.06	0.04	0.07	0.08	0.07	0.03
U	0.05	0.05	0.05	0.31	0.08	0.19	-
ΣREE	2.100	2.515	2.797	4.555	2.800	3.904	2.730
$(La/Yb)_N$	4.065	4.806	4.483	5.443	3.318	4.745	-

Px - pyroxene, Rdn - rhodonite, Mnilv - manganilvaite, Ca - calcite; n.d. - not detected



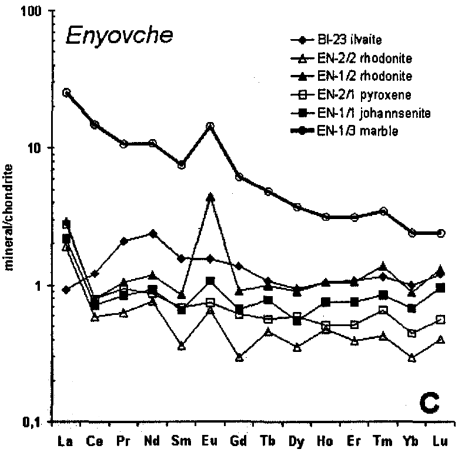


Fig. 4. Chondrite-normalised *REE* pattern for marbles, skarns and their retrograde replacement products in the three studied deposits (a-c). Normalising factors from Sun and McDonough (1989)

Фиг. 4. Хондрит-нормирано разпределение на *REE* в мрамори, скарни и ретроградните заместващи ги продукти от трите изследвани находища (a-c). Фактори на нормиране по Sun & McDonough (1989)

correlate with higher Zn content also found. The distinct decrease of the Sr content, which in the marbles is rather high (135 ppm), is probably related to its selective inclusion in later barite.

Zapadno Gradishte deposit

The *marbles* from the second marble horizon, which host the skarn-ore bodies, exhibit a geochemical pattern similar to the former one (Table 2, Figs. 4b, 5b). The *REE*-content is very low (ΣREE 0.87 ppm). The chondrite-normalised distribution of these elements indicates a marked *LREE*-enrichment with $(La/Yb)_N$ 22.3 and negative Ce and Eu anomalies.

In the zoned skarns (Fig. 3), the *clinopyroxene,* a manganoan hedenbergite, $Ca_{0.91}Mn_{0.40}Fe_{0.55}Mg_{0.14}Si_{1.99}O_6$, and *rhodonite,* $Ca_{0.18}Mn_{0.78}Fe_{0.04}Mg_{0.02}Si_{0.98}O_3$ (5 analyses), show similar patterns with general enrichment with ΣREE 6.81 and 3.44 ppm, respectively. *Bustamite,* $Ca_{1.00}Mn_{1.77}Fe_{0.23}Mg_{0.01}Si_{2.98}Al_{0.01}O_9$ (8 analyses), always replacing skarn pyroxenes,

Table 2. *REE and some trace element concentrations of marbles, skarn- and post-skarn minerals from the Zapadno Gradishte, Enyovche and Byal Izvor deposits, ppm*

Таблица 2. *Концентрации на REE и някои елементи-следи в мрамори, скарни и апоскарнови минерали от находища Западно Градище, Еньовче и Бял извор, ppm*

	Zapadno Gradishte					Enyovche					Byal Izvor
	ZG-11/5	ZG-11/8	ZG-11/2	ZG-11/4	ZG-11/3	EN-1/3	EN-1/1	EN-1/2	EN-2/1	EN-2/2	BI-23
	Marble	Px	Rdn	Bust	Gar	Marble	Px	Rdn	Px	Rdn	Ilv
Sc	0.15	0.75	0.33	0.17	1.56	0.29	0.18	0.18	0.14	0.11	0.57
Co	nd	n.d.	0.20	n.d.	n.d.	n.d.	0.48	0.31	0.90	0.47	n.d.
Ni	n.d.	n.d.	1.01	n.d.	n.d.	n.d.	1.43	0.98	1.42	0.98	n.d.
Ga	0.29	6.06	5.19	0.34	9.90	0.43	5.26	5.87	5.51	6.92	5.99
Ge	0.05	2.38	0.92	0.96	12.15	0.24	3.35	1.30	0.94	0.72	14.89
Rb	0.15	12.60	0.54	0.64	5.38	4.71	0.73	0.70	0.35	0.37	0.37
Sr	270.17	118.86	11.95	25.26	30.51	247.07	8.17	63.40	7.64	7.11	31.46
Y	0.12	2.81	3.56	6.47	5.74	8.57	1.87	2.71	1.36	0.89	6.16
Zr	-	9.77	2.07	6.94	11.55	-	0.86	1.08	0.66	0.72	3.92
Nb	-	0.58	0.10	0.19	0.76	-	0.01	0.04	0.11	0.05	0.06
Mo	-	1.43	n.d.	1.78	0.36	-	n.d.	n.d.	n.d.	n.d.	0.24
Sn	-	0.42	n.d.	0.17	0.21	-	n.d.	n.d.	n.d.	n.d.	0.59
Cs	-	3.62	0.12	0.36	1.85	1.80	0.08	0.10	0.04	0.05	0.15
Ba	30.75	215.45	8.53	8.69	61.11	12.83	4.37	4.33	8.18	3.71	10.84
La	0.25	1.33	0.66	0.27	3.37	5.99	0.52	0.69	0.66	0.45	0.22
Ce	0.35	2.81	0.63	0.66	3.88	9.11	0.44	0.49	0.49	0.36	0.75
Pr	0.05	0.29	0.11	0.14	0.50	1.02	0.08	0.10	0.09	0.06	0.2
Nd	0.10	1.29	0.67	0.77	1.79	5.06	0.44	0.56	0.41	0.36	1.11
Sm	0.02	0.23	0.17	0.24	0.34	1.15	0.10	0.13	0.11	0.06	0.24
Eu	0.01	0.05	0.03	0.04	0.13	0.83	0.06	0.26	0.04	0.04	0.09
Gd	0.02	0.25	0.22	0.33	0.40	1.25	0.14	0.19	0.13	0.06	0.28
Tb	0.01	0.03	0.04	0.05	0.06	0.18	0.03	0.04	0.02	0.02	0.04
Dy	0.03	0.21	0.26	0.35	0.37	0.95	0.14	0.23	0.15	0.09	0.24
Ho	-	0.05	0.08	0.07	0.07	0.18	0.04	0.06	0.03	0.03	0.06
Er	0.03	0.13	0.25	0.18	0.25	0.52	0.13	0.18	0.09	0.07	0.18
Tm	-	0.02	0.04	0.02	0.04	0.09	0.02	0.04	0.02	0.01	0.03
Yb	-	0.11	0.25	0.10	0.17	0.41	0.12	0.15	0.08	0.05	0.17
Lu	-	0.01	0.05	0.01	0.03	0.06	0.02	0.03	0.01	0.01	0.03
Hf	-	0.19	0.05	0.19	0.18	0.00	0.02	0.03	0.03	0.02	0.09
Ta	0.38	0.05	0.00	0.04	0.04	0.59	0.29	0.03	0.03	0.01	0.12
W	0.27	n.d.	0.95	n.d.	n.d.	1.51	162.70	7.45	3.42	6.77	n.d.
Th	0.02	0.16	0.08	0.12	0.10	0.08	0.05	0.06	0.59	0.04	0.00
U	0.19	0.09	0.13	0.15	0.10	0.07	0.09	0.26	0.13	0.03	0.07
ΣREE	0.870	6.810	3.439	3.230	11.400	26.800	2.270	3.127	2.309	1.648	3.640
$(La/Yb)_N$	22.285	8.673	1.932	1.937	14.219	10.480	3.243	3.300	6.312	6.456	0.928

Px - pyroxene, Rdn - rhodonite, Bust - bustamite, Gar - garnet, Ilv - ilvaite; n.d. - not detected

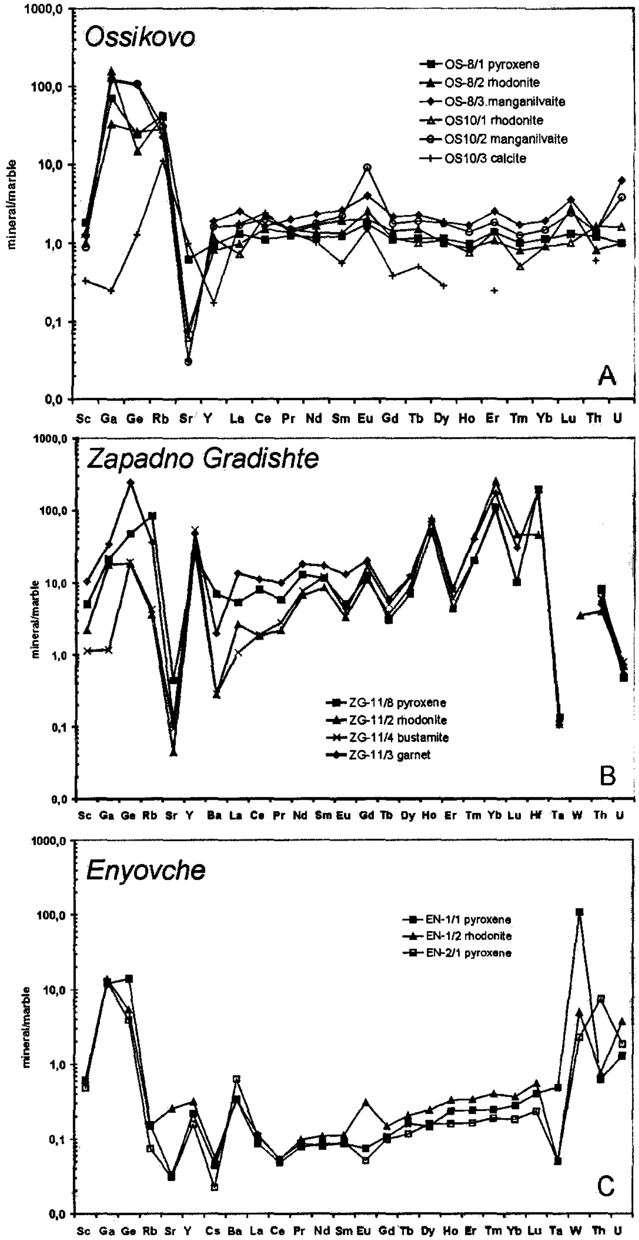


Fig. 5. Marble-normalised contents for *REE* and trace elements from the three studied deposits (a-c)
Фиг. 5. Съдържания на *REE* и на елементи-следи за трите изследвани находища (а-с), нормирани спрямо съдържанията им в изходните мрамори

retains the same general character of the *REE*-distribution, with *ΣREE* 3.23 ppm. *Mn-bearing andradite,* $Ca_{5.79}Mn_{0.40}Fe^{3+}_{3.70}Al_{0.27}Si_{5.91}O_{24}$ and $Ca_{5.65}Mn_{0.44}Fe^{3+}_{2.81}Al_{1.18}Si_{5.90}O_{24}$, is a late-formed garnet that contains 2.77 and 3.18 wt.% MnO in the core and the periphery, respectively. Its *REE* content is higher (*ΣREE* 11.40 ppm), with *LREE* enrichment with $(La/Yb)_N$ 1.94; the Eu-anomaly reaching low positive value. The marble-normalised trace element pattern reveals enrichment in Ga, Ge, Y and *REE* with slightly higher *HREE* and depletion in Sr, Ba, Ta (Fig. 5b).

Enyovche deposit

The skarn-ore bodies of the Enyovche deposit are localised in the thick *marbles* of the Variegated Formation. The rare-earth element pattern (Table 2 and Fig. 4c) differs from that in the marbles in the western limb of the Madan dome. The following more essential differences can be noted:

- the content of rare-earth elements, though sufficiently low, is definitely higher than that in the marbles from the western limb; the total content of *ΣREE* 26.8 is in fact over one order higher and probably can be related to the higher amount of accessory minerals;
- the chondrite-normalised *REE* pattern retains its character; the predominance of *LREE* over *HREE* with $(La/Yb)_N$ 10.5 and a positive Eu-anomaly and a weak negative Ce-anomaly.

The *REE* patterns of *johannsenite,* $Ca_{0.98}Mn_{0.96}Fe_{0.03}Mg_{0.03}Si_{1.99}O_6$ (average of 15 analyses) and *rhodonite* $Ca_{0.21}Mn_{0.78}Fe_{0.03}Mg_{0.01}Si_{0.98}O_3$ (8 analyses) follow the patterns of the marbles (Fig. 4c). However, irrespective of the higher concentrations in the marbles, the contents of rare-earth elements are entirely comparable to those in the other deposits with *ΣREE* 2.27 and 1.65-3.13 ppm, respectively. The light rare-earth elements (*LREE*) predominate with $(La/Yb)_N$ between 3.2 and 6.5. Eu retains its positive anomaly as in the marbles. There is also a relative enrichment in Lu. The marble-normalised patterns (Fig. 5c) show enrichment in Ga, Ge and W. The contents of the other trace elements are considerably lower.

The Mn-bearing *ilvaite* from the Byal Izvor occurrence (Vassileva et al., 2001), located in the eastern part of the region, close to the Enyovche deposit, shows similar characteristics to those of the skarn silicates from this deposit, as also to the considerably Mn-richer manganilvaite from Ossikovo.

Discussion

We shall focus our attention on the behaviour of rare-earth and trace elements in the hydrothermal process without going into a detailed characteristic of these elements in the marbles from the district and the reasons for their differences, which so far are not supported by sufficient systematic data. However, an interesting points can be mentioned: the generally established slope of *REE* pattern with an enrichment of the light over the heavy elements can be the result of pure crystal-chemical control: the largest in size *LREE* (Fig. 6), closest in ionic radius to the only available substitutional sites in calcite structure, the calcite octahedra $^{[6]}Ca^{2+}$, are preferentially incorporated in calcite, whereas the smaller *REE* ions with gradually decreasing ionic radius and increasing size discrepance are included in gradually decreasing amounts. Such distribution have been discussed by Morgan and Wandless (1980) and others.

The main skarn silicate *pyroxenes* and their retrograde products inherit the characteristic distribution of *REE* in the host marbles with general enrichment of light over heavy elements (Fig. 4). This can be explained again by the basic role of Ca in the new-formed silicates (Fig. 6). Ca in this case occupies larger 7-coordinated polyhedra $^{[7]}Ca^{2+}$, acting as favourable sites, easily accommodating the lighter rare-earth elements with largest effective ionic radii (Shannon, 1976; Nicolescu et al., 1998).

The enrichment of post-skarn manganoan silicates and in particular *rhodonite* in Lu, the heaviest rare-earth element, is another interesting phenomenon. In this case Lu, having the smallest effective ion radius, is

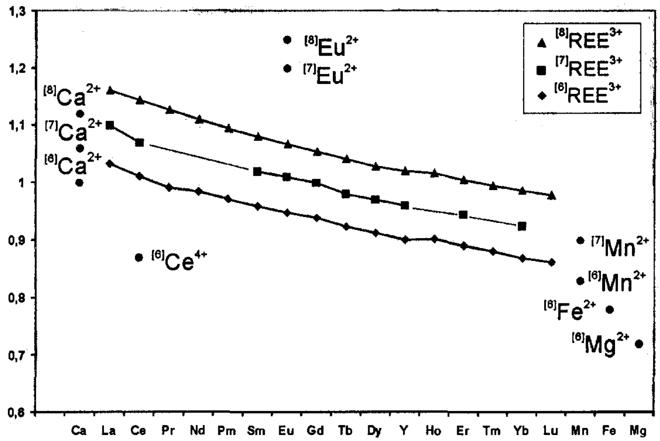


Fig. 6. Effective ionic radii for *REE* and for the main cations of the host rocks, Ca and Mn, in their different coordination polyhedra: $^{[6]}Ca^{2+}$ in calcite, $^{[7]}Ca^{2+}$ and $^{[7]}Mn^{2+}$ in the most skarn and post-skarn silicates (after Shannon, 1976)

Фиг. 6. Ефективни йонни радиуси на *REE* и на главните катиони във вместващите скали, Ca and Mn, в техните различни координационни полиедри: $^{[6]}Ca^{2+}$ в калцита, $^{[7]}Ca^{2+}$ и $^{[7]}Mn^{2+}$ в повечето скарнови и апоскарнови силикати (според Shannon, 1976)

rather close to the manganese in $^{[6]}Mn^{2+}$ which in turn is the largest in the group of the small octahedrally coordinated major cations in pyroxenes and pyroxenoids: Mn^{2+}, Fe^{2+}, and Mg^{2+} (Fig. 6). Thus, manganese silicates and in particular rhodonite, the Mn-richest mineral among them (up to 42-43 wt. %) but also and with a larger $^{[7]}Mn^{2+}$ polyhedron, turns out to be the most suitable host of Lu. Manganilvaite and garnet retain the character of the *REE* distribution and show a certain further total enrichment. The marble-normalised values repeat these specific patterns (Fig. 5). In this case, the whole silicate association traces a pattern close to the initial one.

The chondrite-normalised content of individual *REE* for all of these minerals is not considerably deviating from 1. Evidently, in the discussed lead-zinc deposits, the elements of the *REE* group have very low mobility in the hydrothermal fluids, and during the skarn formation and post-skarn alterations and ore-formation there is only a local re-deposition of these elements derived from the initial marbles. Only the late calcite turns out to be rather depleted with respect to the average levels of *REE* in this post-skarn association. This reflects the even lower content of these elements in the final stages of the process.

In other skarn deposits, the *REE* concentrations in the silicate minerals are often higher. Such e.g. is the case with grandite and hedenbergite from Ocna de Fier in Romania (Nicolescu et al., 1998) which, however, is an intrusion-related contact-metasomatic skarn deposit.

Among the other trace elements in the Rhodope deposits, Sr is considerably more mobile and its content in the marbles is everywhere high (Table 1). Showing a distinct tendency to concentration in hydrothermal barite, Sr depletes the geochemical association of trace elements in the skarn and post-skarn silicates. In all three studied deposits, the analyses of silicates indicate an enrichment of the association of some specific elements: Zr, Hf, Mo, Sn, Ga Ge, etc. This is explained mainly by the presence of dispersed, independently inherited (zircon), or newly formed mineral phases (molybdenite, sphalerite). In fact, different behaviour show mostly the elements of chalcophilic character with their higher mobility in the hydrothermal solutions

Conclusion

The *REE* content in the marbles, which host the metasomatic skarn-ore bodies in the Madan Pb-Zn district, is very low. Due to the relative immobility and inert behaviour of these elements in the hydrothermal process, during the formation of the reduced pyroxene skarns and their subsequent replacement by retrograde silicates, the *REE* content to a large extent is inherited from the initial calcite marbles and is preserved in the later products, reaching a certain weak enrichment. In general, the character of the Ce and Eu anomalies is also inherited. Ca as the main component of all these minerals: $^{[6]}Ca^{2+}$ in the calcite marbles and $^{[7]}Ca^{2+}$in the most silicates ($^{[8]}Ca^{2+}$ in garnets), determine the possibility for *REE* incorporation in their structures. In the high-manganoan silicate minerals, in particular rhodonite, enrichment in Lu is observed, related to the similarities of the effective radii of Lu and Mn^{2+}. The chondrite-normalised values for skarn and post-skarn minerals from the different deposits show similar total *REE* contents. Some of the other trace elements observed, like the chalcophilic Ga, Ge, Mo, Sn, W, are mostly related to ore minerals arisen in the hydrothermal ore-forming process.

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