

MAGNESIAN SKARNS FROM THE DJURKOVO PB-ZN DEPOSIT: MINERAL COMPOSITION AND RETROGRADE ALTERATION

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Abstract

The studied diopside-forsterite skarn from the Djurkovo base metal deposit formed through high-temperature metasomatic processes between dolomitic marble and fluids associated with a thin pegmatite dyke. Early prograde stages involved decarbonation reactions and SiO₂ addition, resulting in diopside and forsterite deposition, followed by phlogopite crystallization. Subsequent retrograde alteration replaced primary minerals with tremolite, serpentine, talc, and chlorite, the latter indicating precipitation temperatures at ~ 260 °C. Mineral assemblages and textures reflect a multistage evolution involving progressive hydration and oxidation (evidenced by troilite/magnetite transformation). Trace element geochemistry reveals incorporation of Li, B, Zn, Ga, V, Cr, Cs, Y, and Nb, generally concentrated in retrograde phases. Despite the lack of economic mineralization, the geochemical signatures of the studied skarn provide insights into fluid evolution and mineral-forming processes and may assist in broader exploration within the Central Rhodopean metallogenic province.

Key words: diopside, olivine, base metal deposits, Central Rhodopes, Laki ore district

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Introduction. Skarn deposits have long been a subject of investigation as a favourable environment for deposition of economic ore accumulations of Fe, Au, Cu, Zn, W, Mo, and Sn [1]. The formation of primary skarns results from regional or contact metamorphism and metasomatic processes involving fluids of various origin (e.g. magmatic, metamorphic, meteoric, marine) and their interaction with carbonate host rocks. The resulting mineral assemblage is mostly presented by calcsilicates such as garnet and pyroxene [2]. A distinctive class of metasomatic rocks, formed by replacement in Mg-rich host carbonate lithology (dolomites/magnesite) and mineral composition dominated by magnesium silicates such as forsterite, diopside, phlogopite is distinguished as magnesian skarn [3].

The present contribution focuses on the mineralogical and geochemical features of magnesian skarns from the Djurkovo base metal deposit, Laki ore district.

Geological setting. Significant polymetallic mineralization of economic importance is concentrated in the Laki ore district, situated in the northern part of the Central Rhodope Mts., south Bulgaria. The Pb-Zn deposits and occurrences in the region, together with those in the Madan, Davidkovo and Ardino districts are part of a large-scale hydrothermal ore province, associated with the Eocene tectono-magmatic evolution of this part of the Rhodope metamorphic complex.

The Laki ore district (Fig. 1) is located along the northern flank of the so-

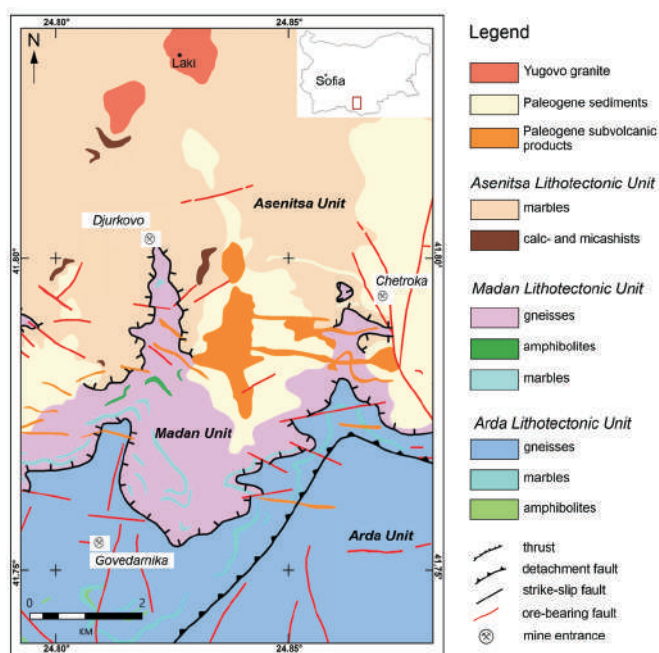


Fig. 1. Simplified geological map of the Laki ore district, modified after [6]

called Central Rhodopean Dome [4] and at the western margin of the Eastern Rhodope Paleogene depression [5, 6]. Base metal deposits of vein and replacement type are hosted by the high-grade metamorphic lithologies (generally biotite gneiss, amphibolite, marble) of the Madan and Arda lithotectonic units of the Rhodope metamorphic complex. The ore mineralization is connected to a system of four major N-NE-trending fault zones: Djurkovo, Govedarnika, Momchil Yunak and Chetroka from west to east. The metamorphic sequence hosts numerous pre-ore hydrothermally altered pegmatites, mostly conformable or crosscutting the metamorphic fabric [7, 8], reaching up to several meters in width. Volcanic rocks related to the Borovitsa caldera are characteristic in the eastern parts of the Laki ore district, (e.g. Chetroka). Historically, in the last 50 years several underground mines were exploited. Two mines are in exploitation presently – Djurkovo and Govedarnika, represented by two different styles of ore mineralization (predominantly vein and replacement, respectively), but with uniform sulphide association of galena, sphalerite, pyrite and occasional chalcopyrite. In the Djurkovo deposit, the ore bodies are predominantly of vein type with differing width (tens of cm to several meters) and lengths reaching several km. The veins are formed by open space filling along fault structures and hosted by the aluminosilicate rocks. Metasomatic ore bodies are formed at the intersection of the fluid-conducting faults with marbles. In the Djurkovo deposit lithologically-controlled carbonate-replacement massive ores (without skarns) dominate, while in Govedarnika skarns are developed in the marbles prior to sulphide deposition, forming the largest Pb-Zn metasomatic skarn-ore accumulation in the Central Rhodopes. The Govedarnika infiltration skarns are composed by Mn-rich silicate association of clinopyroxenes (johannsenite-hedenbergite), pyroxenoids (rhodonite, bustamite), manganilaite [9, 10] acting as favourable host for the overprinted economic mineralization. Despite the widespread distal skarns in the whole metallogenic province of the Central Rhodopes e.g. [11], occasional manifestation of spatially restricted proximal magnesian skarns is observed in several working places in the Djurkovo deposit.

Materials and methods. Representative mineral samples from the magnesian skarns were collected from ore zone 1 at 472 mine level of the Djurkovo Pb-Zn deposit with special attention to the diopside/olivine assemblage boundary. Powder X-ray diffraction was used to determine the minerals prior to other analytical techniques. Mineral relationships and points of interest were described using optical (Leica DM750P, Geological Institute, BAS) and scanning electron microscopy (JEOL JSM-6010PLUS/LA, University of Mining and Geology). Cameca SX100 electron microprobe (Laboratory of Electron Microscopy and Microanalysis, Department of Geological Sciences, Masaryk University, Brno) was applied to determine the chemical composition of the minerals. Analytical conditions in wavelength-dispersive mode include accelerating voltage of 15 kV, a beam current of 4–20 nA and a beam size 2–6 μm . X-ray $K\alpha$ and $L\alpha$ lines in natural and syn-

thetic standards were used: albite (Na), sanidine (K), olivine (Mg), almandine (Si, Al, Fe), wollastonite (Ca), Mn_2SiO_4 (Mn), titanite (Ti), topaz (F), chromite (Cr), fluorapatite (P), barite (Ba), gahnite (Zn), ScVO_4 (Sc, V), vanadinite (Cl). Back-scattered electron (BSE) images were taken on both instruments. Minor and trace element signatures in diopside, olivine, phlogopite, tremolite, serpentine, chlorite, and carbonates were acquired by New Wave Research 193 nm Excimer laser UP-193FX attached to a Perkin-Elmer ELAN DRC-e quadrupole inductively coupled plasma mass spectrometer (Geological Institute, BAS). The LA-ICP-MS system operated at 7–8 Hz repetition rate; spot size of 35 and 50 μm was set. Data were refined based on the external (NIST 610 and 612 glasses) and internal (SiO_2 content from EPMA) standards using SILLS program.

Results. Occurrence. The studied mineralization is developed on both sides of thin subhorizontal pegmatite (10 cm) emplaced conformably in marble (Fig. 2A). Diopside zone above the pegmatite has thickness of up to 5 cm, sharp contacts with the marble and diffusive contacts with pegmatite. Below the dyke, the skarns are presented as alternating pyroxene bands with pockets of irregularly-shaped dark green to grass green olivine grains (up to 0.5 cm) in marble (Fig. 2B). Closely associated mica flakes are also typical for the olivine-carbonate lenses.

Mineral composition. Based on the EPMA and X-ray diffractometry data the studied magnesian skarns are generally composed by diopside, phlogopite and forsterite. Diopside forms massive aggregates of short prismatic sub- to euhedral crystals with interstitial later calcite. Irregularly shaped olivine crystals and their clusters in the marble are generally associated with phlogopite and abundant anhedral patches of dolomite (e.g. Fig. 2F). The optical microscopy and BSE images (Fig. 2) revealed overprinted retrograde alteration after the clinopyroxene, olivine and mica. Diopside/forsterite direct contact has not been observed, instead the boundary between them is marked by retrograde products as amphibole radiating aggregates and talc veinlets (Fig. 2C, F, G). Phlogopite occurs either as single crystals attached to olivine (Fig. 2F, G) or in the carbonate matrix, or as aggregates of elongated flakes (Fig. 2E, I, J). Subsequent alteration by chlorite is evident. All of the studied olivine metasomatic grains are fractured and replaced by a crack-filling network of serpentine-group minerals (Fig. 1D, H). Serpentine alteration results from the retrogression of olivine; X-ray powder diffraction patterns reveal presence of both chrysotile and lizardite. Their occurrence is marked also by distinctive magnetite grains and aggregates, observed only in the serpentine volume. Troilite (FeS), on the other hand, occurs in the carbonate matrix or among the individual olivine grains. The larger troilites were transformed to magnetite (Fig. 2K) indicating conditional changes.

Chemical composition. The contents of the major elements in the minerals are presented in Table 1. Compositional variations in the crystal structures of the minerals are mainly attributed to key substitutions of Mg by Mn, Fe^{2+} and Al (e.g. diopside, olivine, phlogopite); Mg by Ti (e.g. phlogopite) and occasionally of

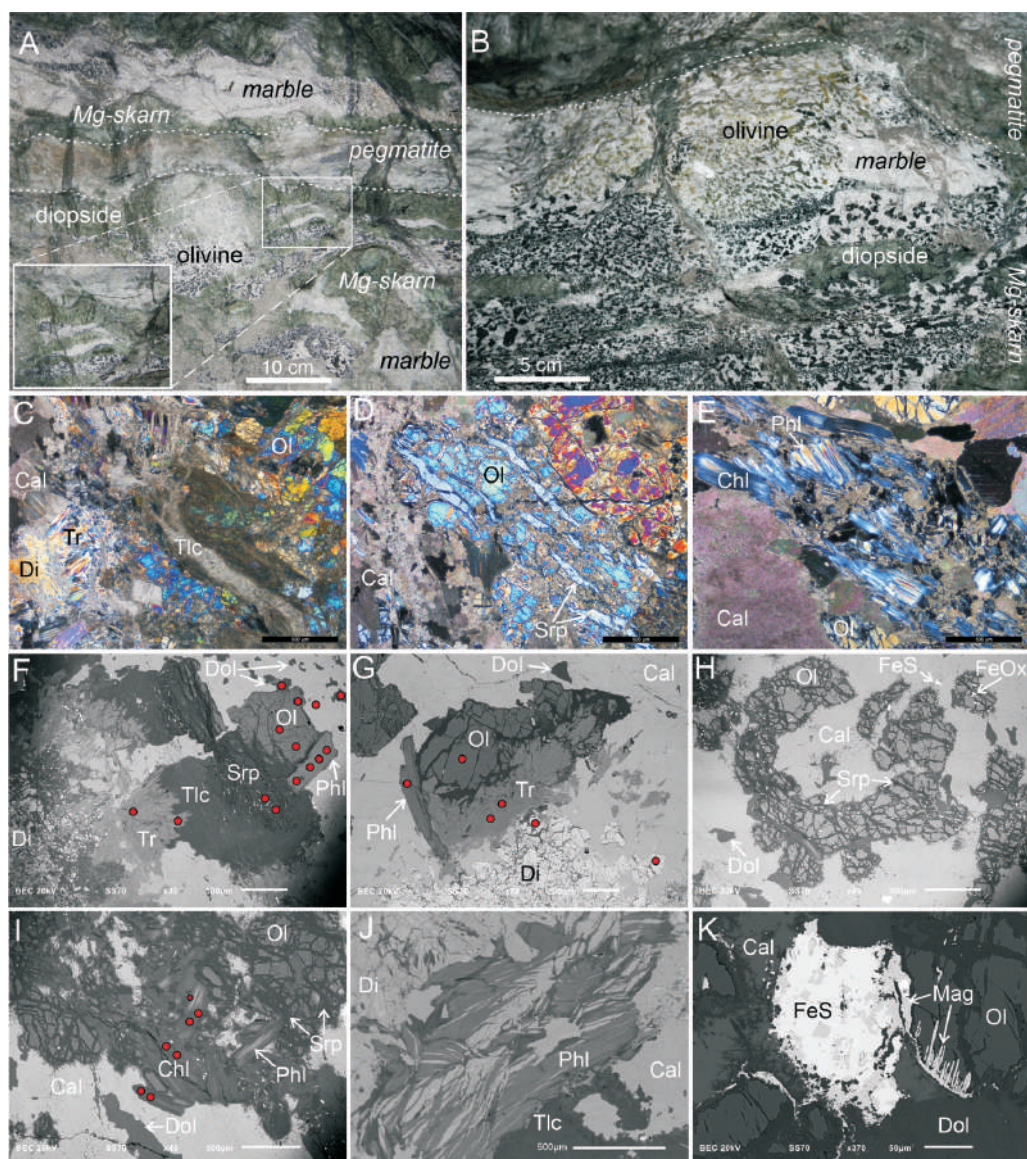


Fig. 2. Mineral association of the magnesian skarns: A–B) occurrence of the diopside bands and olivine pockets in marble on both sides of pegmatite dyke; C–E) optical microscopy in CPL; C) the boundary between diopside and olivine zones; D) serpentine network after olivine; E) phlogopite replaced by chlorite; F–K) back-scattered electron images (BSEI) of the F) diopside/olivine boundary with secondary tremolite, talc, serpentine; G) assemblage of olivine, phlogopite, tremolite and diopside; H) irregular metasomatic olivine grains replaced by serpentine and magnetite; I) phlogopite/chlorite replacement in between serpentinized olivine; J) phlogopite associated with diopside; K) troilite (FeS) replaced by magnetite in the olivine zone. Abbreviations [12]: Cal – calcite, Di – diopside, Dol – dolomite, Mag – magnetite, Ol – olivine, Phl – phlogopite, Srp – serpentine, Tlc – talc, Tr – tremolite. Red dots correspond to LA-ICP-MS analytical points

T a b l e 1
Representative chemical composition data of the studied minerals in selected analytical points

mineral analytical points	diopside		forsterite		phlogopite		tremolite		clinocllore			talc	chrysotile
	Di 21	Di 23	Ol 33	Ol 49	Phl 18	Phl 39	Tr 54	Tr 55	Chl 13	Chl 15	Tlc 16		
K ₂ O, wt %					9.95	10.47	0.11	0.09		0.02	0.02	0.01	Srp
Na ₂ O	0.03	0.05			0.08	0.11	0.14	0.17	0.02	0.03	0.03	0.01	
CaO	25.40	25.79	0.02	0.01	0.01		14.03	13.68	0.03	0.01	0.05	2.13	
MgO	15.14	16.83	52.47	51.79	27.09	26.85	24.08	23.42	25.81	25.53	29.10	41.16	
MnO	0.25	0.11	0.18	0.18		0.03			0.19	0.22	0.03	0.12	
FeO _{tot}	4.57	2.01	5.44	5.82	1.73	1.06	0.56	0.58	10.54	10.38	1.50	1.85	
ZnO	0.13	0.12	0.11	0.08		0.10			0.12	0.07	0.03		
Al ₂ O ₃	0.45	0.11	0.01		11.58	11.50	0.27	0.27	19.00	19.44	0.14	0.10	
SiO ₂	53.93	54.86	41.51	42.09	42.88	43.16	58.87	58.60	30.30	30.30	62.41	43.35	
P ₂ O ₅		0.02	0.03	0.04		0.01	0.03					0.01	
TiO ₂	0.03	0.01	0.03	0.01	0.06	0.21	0.05	0.02			0.01		
V ₂ O ₃								0.00					
Cr ₂ O ₃			0.06		0.06	0.03			0.01	0.02			
NiO			0.05					0.01		0.02			
BaO	0.06				0.04	0.04		0.03					
F	0.11	0.07			1.76	1.87	0.48	0.41	0.04	0.03	0.23		
Cl		0.01	0.02	0.01	0.02		0.00	0.02			0.01		
total	100.10	100.00	99.93	100.02	95.26	95.44	98.62	97.30	86.06	86.08	93.55	88.75	

T a b l e 1
Continued

mineral analytical points	diopside		forsterite		phlogopite		tremolite		clinocllore			talc	chrysotile
	Di 21	Di 23	Ol 33	Ol 49	Phl 18	Phl 39	Tr 54	Tr 55	Chl 13	Chl 15	Tlc 16		Srp
K, <i>apfu</i>					0.903	0.949	0.018	0.016		0.005	0.001		0.001
Na	0.002	0.003			0.011	0.014	0.035	0.045	0.008	0.010	0.003		0.001
Ca	1.004	1.007	0.001		0.001		2.035	2.006	0.004	0.001	0.003		0.105
Mg	0.832	0.915	1.882	1.855	2.872	2.843	4.859	4.779	3.781	3.732	2.810		2.822
Mn	0.008	0.003	0.004	0.004		0.002			0.016	0.018	0.002		0.005
Fe ²⁺	0.141	0.061	0.110	0.117	0.103	0.063	0.064	0.067	0.767	0.735	0.081		0.071
Fe ³⁺									0.099	0.116			
Zn	0.003	0.003	0.002	0.001		0.005			0.009	0.005	0.001		
Al	0.020	0.005			0.971	0.963	0.043	0.044	2.201	2.246	0.011		0.006
Si	1.989	2.000	0.999	1.011	3.049	3.066	7.968	8.023	2.978	2.971	4.042		1.994
P							0.002						
Ti	0.001				0.003	0.011	0.005	0.002			0.001		
V													
Cr			0.001						0.001	0.002			
Ni			0.001					0.001		0.001			
Ba													
F					0.396	0.419	0.206	0.177	0.023	0.021	0.047		
Cl					0.002		0.001	0.004			0.001		

Mg by Zn (e.g. diopside, olivine, chlorite). Apart from exchanges in the octahedral site, Al^{3+} for Si^{4+} heterovalent substitutions are exhibited in the tetrahedral position of some layered silicates (e.g. Tschermak substitution in clinocllore), as well as variations in the hydroxyl part, namely F-, Cl-contents.

The set of trace elements across most minerals is generally similar (Table 2, Fig. 3). Diopside, forsterite, and serpentine typically contain significant amounts Zn (hundreds of ppm), while its quantity in other minerals decreases to only tens of ppm. Elevated incorporation of V and Cr are characteristic of phlogopite (103–

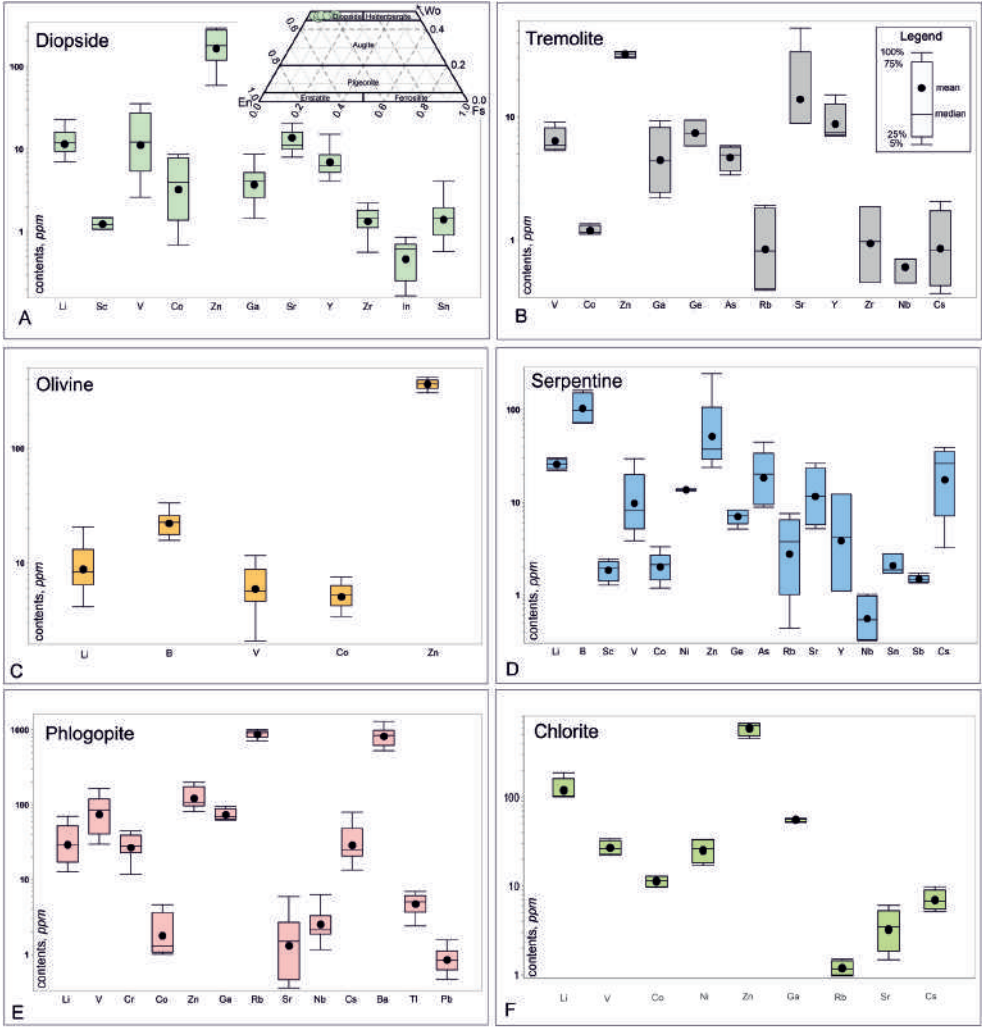


Fig. 3. Box and whisker plots showing the distribution of trace elements in the main minerals and in their alteration products: diopside to tremolite; olivine to serpentine, and phlogopite to chlorite. Inset in A) corresponds to ternary classification of pyroxenes in wollastonite-enstatite-ferrosillite compositional space

T a b l e 2

Trace element incorporation in the studied minerals

Mineral	diopside		tremolite		forsterite		serpentine		phlogopite		clinochlore		dolomite		calcite/ marble	
Element, ppm	$n = 14$		$n = 7$		$n = 12$		$n = 7$		$n = 16$		$n = 14$		$n = 4$		$n = 4$	
	min	max	min	max	min	max	min	max	min	max	min	max	min	max	min	max
Li	7.00	22.7	bdl	3.40	6.60	13.6	15.3	20.8	12.6	70.2	99.9	187	bdl	bdl	bdl	bdl
Be	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
B	bdl	bdl	bdl	bdl	18.4	33.4	49.6	112	bdl	bdl	33.7	94.9	bdl	7.26	bdl	bdl
Sc	bdl	1.35	bdl	1.70	bdl	1.16	0.884	1.68	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
V	2.63	35.5	5.83	9.10	2.08	11.6	2.68	20.4	39.2	230	34.0	169	1.16	1.76	bdl	bdl
Cr	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	144	35.2	144	bdl	bdl	bdl	bdl
Co	1.40	8.68	1.120	1.36	5.42	7.52	0.826	2.310	0.873	4.09	0.701	12.8	bdl	bdl	bdl	bdl
Ni	bdl	9.92	bdl	bdl	bdl	14.2	bdl	9.697	bdl	bdl	bdl	33.1	bdl	bdl	bdl	bdl
Cu	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2.92	bdl	3.56	bdl	bdl	bdl	bdl
Zn	70	291	30.1	34.0	362	420	16.6	169	17.8	194	12.0	671	10.40	13.4	bdl	bdl
Ga	1.45	8.72	2.19	9.31	bdl	bdl	bdl	3.33	42.9	95.5	30.0	57.6	bdl	bdl	bdl	bdl
Ge	bdl	bdl	bdl	9.39	bdl	13.0	3.57	5.76	bdl	6.59	bdl	bdl	bdl	bdl	bdl	bdl
As	bdl	3.45	3.38	5.82	bdl	bdl	6.13	30.8	bdl	bdl	bdl	8.033	bdl	2.89	bdl	2.89
Se	bdl	bdl	bdl	11.5	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Rb	bdl	bdl	0.426	1.91	bdl	bdl	1.63	5.258	169	1008	1.51	127	bdl	0.18	bdl	bdl

* bdl refers to measured elements which are below detection limits

T a b l e 2
Continued

Mineral	diopside		tremolite		forsterite		serpentine		phlogopite		clinochlore		dolomite		calcite/ marble	
Element, ppm	$n = 14$		$n = 7$		$n = 12$		$n = 7$		$n = 16$		$n = 14$		$n = 4$		$n = 4$	
	min	max	min	max	min	max	min	max	min	max	min	max	min	max	min	max
Sr	9.98	20.8	8.86	9.01	bdl		4.42	18.2	0.472	5.97	0.985	8.97	100	109	198	210
Y	5.29	15.1	6.99	15.1	bdl		bdl	8.44	bdl		bdl		1.07	1.31	6.38	15.5
Zr	0.562	2.22	bdl	1.86	bdl	1.21	bdl	0.500	bdl		bdl	1.79	bdl	bdl		bdl
Nb	bdl	0.659	0.445	0.700	0.348	1.57	0.223	0.706	1.16	14.6	0.716	4.92	bdl	0.155	bdl	
In	0.175	0.859	bdl		0.085	0.277	bdl	0.364	bdl		bdl		bdl		bdl	
Sn	0.921	4.06	bdl	0.904	bdl	0.589	bdl	1.20	bdl		bdl		bdl		bdl	
Sb	bdl	0.752	bdl	0.976	bdl		0.941	1.19	bdl		bdl		bdl		bdl	
Cs	0.190	1.15	0.365	2.05	bdl		10.9	27.1	9.86	79.9	5.15	35.3	bdl		bdl	
Ba	bdl		bdl	0.778	bdl		bdl	1.36	102	1294	2.07	94.8	bdl	0.891	bdl	9.02
Σ REE	4	14	3.619	7.53	0	0.442	0.256	1.65	0	0.828	0	1.08	3.81	5.09	10.0	18.9
W	bdl		bdl	1.02	bdl		0.525	2.16	bdl		bdl		bdl		bdl	
Tl	bdl		bdl		bdl		bdl		2.41	10.2	bdl		bdl		bdl	
Pb	0.963	3.11	bdl		bdl		bdl	0.570	bdl	1.11	bdl		2.17	3.09	bdl	7.26
Th	bdl		bdl		bdl		bdl		bdl	0.642	bdl	0.230	bdl		bdl	
U	bdl	0.294	0.116	0.426	bdl		bdl	0.188	bdl	0.183	bdl		bdl		bdl	

* bdl refers to measured elements which are below detection limits

230 ppm V; up to 143 ppm Cr) and overprinted chlorite compositions (140–167 ppm V; 98–103 ppm Cr), whereas other minerals contain lower amounts of V (up to 35 ppm in diopside) and none Cr. In contrast, chlorite in the diopside zone is characterized by increased Li (100–180 ppm), Zn (450–665 ppm), Ga (50–57 ppm). Although Co concentration remains low (below 10 ppm), it is consistently present in all minerals. Relatively constant content of Li (tens of ppm) is measured in all minerals, except for tremolite. Gallium is present throughout the whole association excluding forsterite, and reaches particularly high levels in phlogopite (43–95 ppm) and chlorite (29–57 ppm). Despite boron being generally incompatible with the olivine structure, forsterite and especially its serpentine alteration exhibit notable B-incorporation ranging between 18–33 and 40–111 ppm, respectively. Rubidium, Cs and Ba are distinctly present in phlogopite and, to lesser extent, in chlorite (Table 1). On the other hand, Sr dominates in carbonates (both calcite and dolomite), but characterizes the signatures of diopside, tremolite and serpentine as well. Traces of Y (below 20 ppm) are revealed particularly in tremolite and diopside being also typical for the host carbonate matrix (marble and to dolomite). Niobium and Tl are notably enriched in phlogopite (up to 10 ppm), with lower concentrations also observed in chlorite. Serpentine composition is additionally characterised by incorporation of tens of ppm As and several ppm Ge, Sn, Sb. Rare earth elements are detected as insignificant content in diopside and tremolite with average total amounts below 10 ppm. Concentrations in the host marble reach ΣREE of 18 ppm, mostly represented by La (4.29 ppm), Ce (7.79 ppm), and Nd (3.42 ppm) incorporation. Similar signature but with lower contents is characteristic of the dolomite.

Discussion and conclusions. The primary minerals in the skarn association are replaced by a retrograde hydrated association presented by tremolite, serpentine and later talc, chlorite. Based on the chemical composition of the chlorite, the calculated temperature of its deposition is 250–270 °C [13]. This temperature range corresponds to the formation of the alteration assemblage. The initial metasomatic processes took place in reduced conditions evidenced by the co-genetic troilite. The observed mineralogical transformations during the cooling and hydration of the earlier high-temperature minerals typically involve oxidation as suggested by the occurrence of the magnetite alteration on troilite (e.g. Fig. 2K).

Although most magnesian skarns generally form by interaction of silicate melts or hydrothermal fluids in Mg-rich protolith [3] such as dolomite (or magnesite), the studied skarn association occurs within impure marble host containing localised patches of $\text{CaMg}(\text{CO}_3)_2$. Field relationships and spatial position (Fig. 2A, B) indicate that the studied skarns may be classified as exoskarns formed at the contact with thin, hydrothermally altered pegmatite dyke. Pegmatite emplacement might have triggered metasomatic replacement and skarn formation via diffusion of Si, Al and K in hydrous solution into the host marble. The min-

eralogical and geochemical data indicate a multistage evolution of the skarns, characterized by an early high-temperature metasomatic assemblage followed by progressive retrograde hydration and oxidation. In the prograde stage dolomite from the impure marble has been consumed at high temperature by decarbonation reactions with SiO₂ (either originally quartz in the marble or SiO₂ from the pegmatite) to produce diopside ($\text{Dol} + \text{Qtz} = \text{Di} + \text{CO}_2$) and forsterite ($\text{Dol} + 0.5\text{Qtz} = \text{Fo} + \text{Cc} + \text{CO}_2$) [14]. The skarn exhibits a primitive zoning pattern, with diopside bands occurring adjacent to the pegmatite and contiguous forsterite zone extending outward. During the second stage, devolatilization of the pegmatite and associated fluid migration led to the formation of phlogopite within the olivine zone ($3\text{Dol} + \text{Kfs} + \text{H}_2\text{O} = \text{Phl} + 3\text{Cc} + 3\text{CO}_2$). Tremolite precipitation after diopside ($5\text{Di} + \text{H}_2\text{O} + 3\text{CO}_2 = \text{Tr} + 3\text{Cc} + 2\text{Qtz}$) possibly coincides with mica deposition in time. The retrograde stage finished with serpentine, talc and chlorite representing the latest alteration products of the primary minerals.

The trace element geochemistry shows distinct elemental partitioning among mineral phases. Diopside, forsterite, and serpentine are enriched in Zn, while phlogopite and chlorite accommodate elevated levels of V, Cr, and Ga. While occurrence of Cr- and V-bearing minerals in marbles, dolomites and skarns is rather common in metasedimentary sequences [15], the influence of the pegmatite emplacement is evidenced by the measured traces of Y and LREE in the chemical composition of the host marble. Lithium, B and Cs are variably distributed across the skarn assemblage, with B and Cs being notably enriched in serpentine after olivine. The presence of trace elements such as Nb, Tl, As, and REE – although in low concentrations – provides additional insights into fluid compositions and metasomatic processes during both prograde and retrograde stages.

Compared to numerous other Mg-skarns mostly of diopside-dominated or diopside-andradite composition [16] observed during the extensive field experience and prior observations in the Djurkovo base metal deposit, the studied skarn is unusual due to its olivine-bearing composition and direct spatial relationship with pegmatite. It is more likely that most of these abovementioned Mg-rich bodies were formed via infiltration-driven reactions and penetration of Mg-rich fluids rather than diffusive exchange. Supporting that, distal johannsenite-hedenbergite infiltration skarns are characteristic of the whole region of the Central Rhodopean polymetallic deposits having significant economic importance by hosting rich sulphide ore bodies [9,11]. In contrast, the studied and the observed in the Djurkovo deposit Mg-skarns are barren and spatially restricted, but their occurrence provides valuable insights into the mineral forming processes in the deposit and in the Central Rhodopean metallogenic province in broader sense.

Overall, the mineralogical and geochemical characteristics of the studied Mg-skarn system point to a complex multistage evolution involving high-temperature metasomatism associated with pegmatite emplacement, followed by lower-tem-

perature retrograde alteration. The textural relationships, element distribution patterns, and secondary phase development reflect dynamic physicochemical conditions during skarn formation and cooling.

The studied magnesian skarn exhibits moderate enrichment in several critical and strategic elements, notably Li, B, Zn, Ga, V, Cr, Cs, and Nb, with most of these elements hosted in retrograde alteration phases (chlorite, serpentine, talc, phlogopite). This reflects a fluid-driven metasomatic system influenced by pegmatite emplacement, which introduced incompatible and volatile elements into the impure marble host. While the studied skarn in the base-metal Djurkovo deposit is barren in terms of ore mineralization, its trace element composition reveals valuable geochemical footprints of fluid evolution, with potential relevance for vectoring towards mineralized zones in broader exploration contexts.

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