GENESIS OF VEIN-STOCKWORK CRYPTOCRYSTALLINE MAGNESITE FROM THE DINARIDE OPHIOLITES

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ABSTRACT

Vein and stock-work cryptocrystalline magnesite deposits, known also as Kraubath type, Gelmagnesite, and Khalilovo type, are widespread in the Tethyan ophiolites from the Alps to the Zagros mountains, including the Dinarides, but also in other ophiolite suites like California, etc. Thirteen samples from the magnesite deposits of the Dinaric and Vardar zone ophiolite belts were analyzed for C- and O-isotopes, major and trace elements, and REE. Genesis of cryptocrystalline magnesite has received two controversial interpretations, involving circulation of Mg-bearing ore fluids, "*per ascendum*" or "*per descendum*" mechanisms. Stable isotope data on C- and O-isotopes in magnesite deposits show significant positive correlation along the light-heavy isotope ratio from vein to stock-work and sedimentary type ore bodies. The thirteen new samples confirmed the same regularity, as a rule for cryptocrystalline magnesite. It should be stressed that there are some exceptions, marked by different isotope patterns, represented by deposits located close to the products of the Tertiary volcanic activity. This paper brings arguments both in favor and against the two genetic models, supported by the new geochemical data. The authors favour, however, the *per descendum* model, stating generation beneath the lateritic weathering crusts, which covered a wide area of the obducted ophiolites, subjected to warm, humid tropical climate in the Early Cretaceous. The laterite crusts acted as a chromatographic column separating immobile elements from mobilized magnesia in solution, which percolating down through a fracture system, deposited magnesite as a result of increased pH. The self refining of ore forming fluids produced almost monomineralic magnesite veins, with or without selvages. The fractionation of light C- and O-isotopes in magnesite needs isotopic light CO_2, commonly interpreted as a derivate of deep seated decarboxylation of organic rich sediments. However, this behaviour of light C- and O-isotopes on a regional scale can be convincingly explained also by closed/semiclosed fractionation between atmospheric CO_2 and magnesite in the descending fluid, controlled by the Rayleigh equation.

INTRODUCTION

Different genetic types of magnesite deposits are spatially related to the ophiolite complexes of the Internal Dinarides (Fig. 1). The Dinaric magnesites from different localities have been described in numerous papers (Hiessleitner, 1934; Donath, 1955; 1957; Ilić Sen., 1959; Ilić Jr., 1964; 1968; 1969a; 1969b; 1983;1988; Zekić, 1972; Petrov et al., 1979; 1980; Vakanjac and Tomanec, 1982; Lapčević, 1982; 1988). Stable isotope data on the magnesite deposits of Strezovac, Beli Kamen, Bela Stena, Rvati and Trnava-Zimovnik, (Ilić Jr. and Popević, 1970) were not included in the genetic interpretation due to the high dispersion of values. More advanced stable isotope data were published by Vakanjac and Tomanec (1982), Schroll et al. (1986), Sunarić-Pamić and Pamić (1988), Kralick et al. (1989), Fallick et al. (1991) and Popević et al. (1996). Jurković and Pamić (2003) synthesized the increasing number of data (Ilić Jr., 1964; 1968; 1969a; 1969b; Vakanjac and Tomanec, 1982; Sunarić-Pamić and Pamić, 1988; Fallick et al., 1991; Jurković, 2000; 2001), and presented an overview of distinguished genetic groups, among the Dinaridic magnesite deposits. The following groups were established: I. Konjuh, Kopaonik, Goleš (Kraubath) vein type; II. Oshve hydrothermal vein type; III. Ražana, Ćosovac, Mramor stockwork type; IV. Miokovac, Beli Kamen stockwork subtype; V. Mušići, Greiner talc-breunnerite type; VI. Šilopaj-Nevade, Branešci, sedimentary type; VII. Bela Stena, Kamenica hydrothermal-sedimentary type; VIII. Janok-Parlog, Miocene fossil detrital type; IX. Badanj-Kukavica detrital type; and X. Glavica infiltration type below the weathering crust (*per descendum*). The classification is primarily based on geological criteria, shape of ore bodies, ore texture, structure, parageneses, etc. Table 1 summarizes 114 published carbon and oxygen isotope data on samples collected from 36 different magnesite deposits located in Bosnia, Serbia and Kosovo (104 magnesite, 7 dolomite, and 3 calcite samples). Classification is grounded on a wide spectrum of the existing interpretations, isotope data, however, simplify and reduce the number of groups to those which fit well into the regression line

$$\delta^{18}O = 0.508\ \delta^{13}C + 32.3$$

established by Fallick et al. (1991) and the ones with possible relation to Tertiary magmatism, like Oshve, vein type II, and Mušići-Greiner, talc-breunerite type VI (Sunarić-Pamić and Pamić, 1988; Jurković and Pamić, 2003). The obtained regression line, which includes C- and O-isotope data of magnesite from the Kraubath vein deposits (n = 10), in the Bosnian Dinaric ophiolites, $\delta^{18}O = 0.409\ \delta^{13}C + 31.4$ (Fig. 2), confirms the regularity established by Fallick et al. (1991). The slight declination of the composite Dinaride regression line is caused by lack of discrimination in the samples from Northern Bosnia, which might belong to different genetic groups.

The present investigation includes carbon and oxygen isotope data, trace elements and REE geochemistry determined on thirteen new samples of cryptocrystalline magnesite from the Dinaric magnesite deposits. A major aim was to accomplish and improve discrimination among the magnesite types, and better define their genesis. The new data have been used to create a regression line $\delta^{18}O = 0.483\ \delta^{13}C+33.4$, supported by a limited but sufficient number of measurements, n = 13, with r = 0.89 (Fig. 2), which follows the streamline of the regression determined by Fallick et al. (1991).

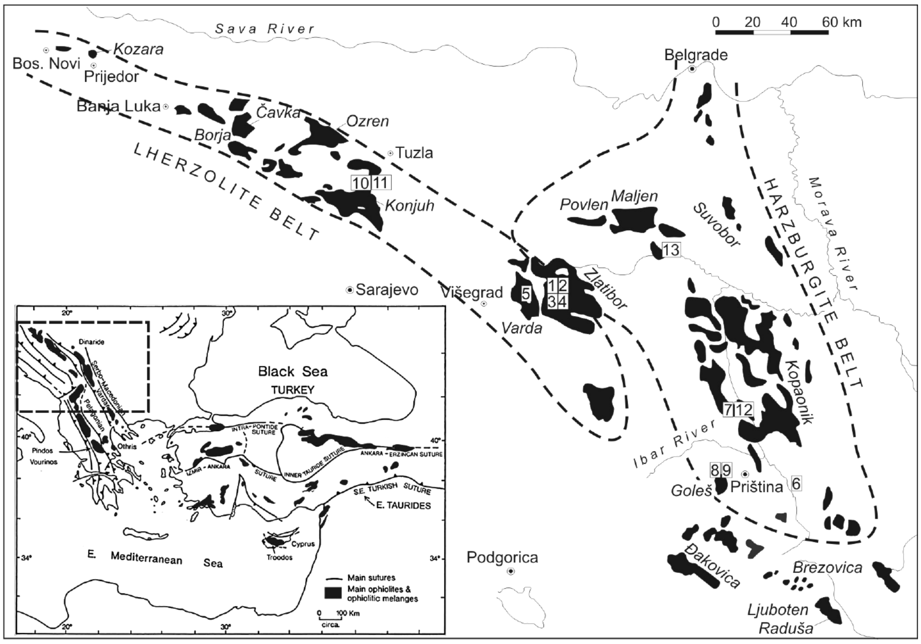

Fig. 1 - Location of the thirteen investigated magnesite deposits in the Dinaride and Vardar ophiolite belts marked by squares and appropriate numbers from Table 2. A loose predominance of harzburgite or lherzolite rock compositions in the ophiolite belts is shown on the map (Pamić and Jurković, 1997).

Table 1 - Summarized carbon and oxygen isotope data of the samples collected from 36 different magnesite deposits and accompanying dolomite and calcite classified in the genetic groups located in Bosnia, Serbia and Kosovo.

Genetic type	*n*	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)
I. Konjuh, Kopaonik; vein type	48	−7.0 to −15.1 (−12.2)	24.1 to 28.4 (26.2)
II. Oshve; hydrothermal vein type	15	0.3 to 5.2 (3.1)	17.9 to 23.2 (20.7)
III. Ražana, Mramor, Ćosovac; stockwork type	11	−7.1 to −11.6 (−8.7)	26.3 to 28.5 (27.5)
IV. Miokovac, Beli Kamen; stockwork subtype	6	2.8 to 4.3 (3.2)	36.1 to 36.2 (36.2)
V. Mušići Greiner talc–breunnerite type	1	1.3	26.1
VI. Šilopaj, Nevade, Branešci sedimentary type	6	−5.1 to −5.6 (−5.3)	27.2 to 31.5 (28.9)
VII. Bela Stena, Kamenica hydrothermal-sedimentary type	11	−2.0 to 4.3 (2.2)	26.2 to 35.9 (31.8)
VIII. Parlog, Janok fossil detrital type	6	−2.2 to 0.2 (−1.1)	29.6 to 33.4 (31.5)
Čerenje *dolomite*	1	0.0	32.5
Kremna *dolomite*	1	3.9	30.3
Ražana *dolomite*	2	−2.0 to −2.1 (−2.1)	−32.1 to −32.1 (−32.1)
Branešci *dolomite*	3	−8.0 to −9.0 (−8.5)	25.5 to 25.7 (25.6)
Kremna *calcite*	3	2.9 to 4.2 (4.0)	25.5 to 27.6 (26.8)

Number of measurements in each genetic group is ***n***. The group mean values are in parentheses and two digits represent their minimum and maximum values.

GEOLOGICAL SETTING, AND STYLE OF MINERALIZATION

Numerous magnesite deposits are spatially and genetically related to the Dinaric ophiolites. A variety of genetic types, from hydrothermal, hydrothermal-sedimentary, sedimentary, products of ophiolite weathering below the laterite crusts *per descendum*, to paleo and recent detrital sedimentary type, are present within all ophiolites units of the Dinarides *sensu stricto*, and Western and Central Vardar zone. Their earliest formation age is constrained by the time of ophiolite emplacement as thrust sheets over the mélange in the Early Cretaceous. The favorable climate conditions in the Early Cretaceous facilitated widespread formation of lateritic weathering crusts, and infiltration processes, forming ramifying magnesite veinlets and stockwork beneath. The upper time limit of the intensive magnesitization of ophiolites meets the timing of the Miocene collisional-postcollisional magmatism. Its thermal impact and hydrothermal activity affected ophiolite complexes, giving rise to comparatively similar magnesite types. Both processes produced nearly equivalent structures, textures and ore body shapes.

The thirteen new samples of cryptocrystalline magnesite (Kraubath type, Gelmagnesite: Redlich, 1909; Pohl, 1990; Khalilovo type magnesite: Petrov et al., 1979; 1980) were selected as representatives of the following deposits: Čajetina, Kose, Krive Strane, Ćave, Mokra Gora (Zlatibor Mt.), Trnava and Bela Stena (Raška, Kopaonik Mt.), Miličevci (Čačak), Goleš and Kamenica (Kosovo), Banovići 1 and Banovići 2 (Konjuh Mt.). Their coordinates, geographical location (district), deposit type, carbon and oxygen isotopes, are presented in Table 2 and their characteristics are described below.

- The Zlatibor ore field occurs in an area including the harzburgitic/lherzolitic massifs and the Neogene lacustrine basins, near the massifs. The ore deposits, vein type I, stockworks type III, are spatially related to the weathering crusts (Fig. 3). The classification of the veins, stockworks and infiltration groups, seem not to be enough discriminative at present, lacking convincing criteria, and rising the question on whether type I and type III are products of hydrothermal activity, or have derived from a deep weathering infiltration, *per descendum* (type X). Absence of magmatism in the Zlatibor area favors the latter mechanism. Presence of boron minerals or elevated boron content in the sedimentary deposit of the Kremna basin (searlesite, Na,B(SiO_3)2; Ilić Jr., 1969b; Obradović et al., 1996) are interpreted as a sign of their hydrothermal nature. However, boron rich sediments are not necessarily originated by hydrothermal fluids, but

Fig. 2 - Diagram shows carbon and oxygen isotope data in the Dinaric magnesite deposits. The fields designated by Roman numerals in the rectangular polygons, represent the genetic groups in Table 1. They are constrained by maximum and minimum values of the groups, and the squares with Roman numerals are their averages. Fallick et al. (1991) constructed the regression "mixing line": $\delta^{18}O = 0.508\ \delta^{13}C + 32.3$, between two end members of CO_2 reservoirs, the one with low $\delta^{18}O$ and $\delta^{13}C$ in ascending hot groundwater (HODC) with organically derived CO_2, and the other with high $\delta^{18}O$ and $\delta^{13}C$, in low-temperature, meteoric water (AMC) with atmospheric CO_2. The 13 new selected samples from this research (Jurković et al., 2012), designated by symbols, follow the regression line $\delta^{18}O = 0.482\ \delta^{13}C + 33.4$. All compiled data are along the composite regression line $\delta^{18}O = 0.409\ \delta^{13}C + 31.4$, including those from the North Bosnian hydrothermal magnesite.

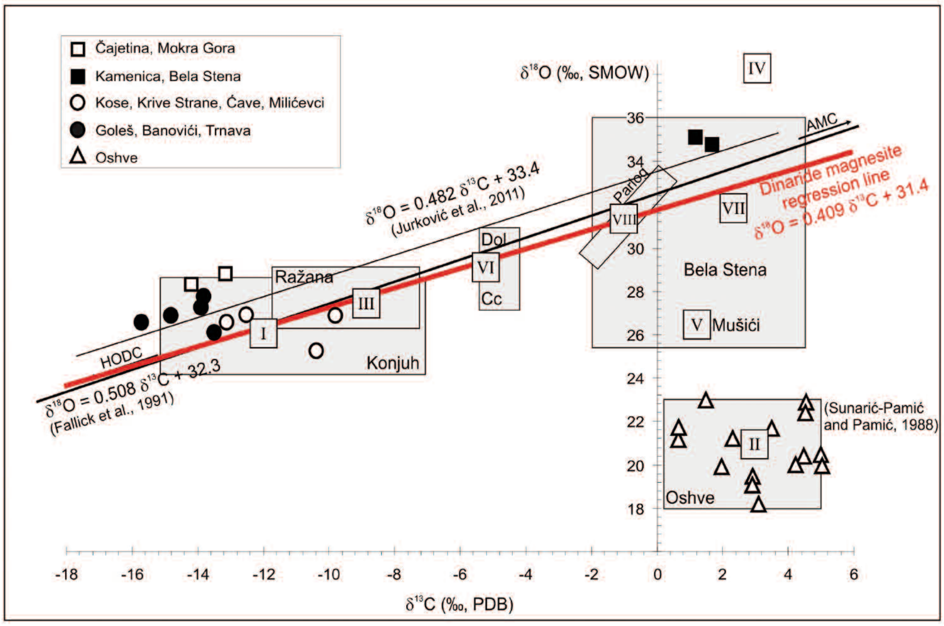

Fig. 3 - Magnesite veins, 1 m thick, developed below the stock-work magnesite mineralisation, Čajetina deposit, Zlatibor Mt.

rather by diagenetic processes in tuffaceous sediments in the saline-alkaline lakes (Sheppard and Gude, 1973; Obradović and Dimitrijević, 1987; Stamatakis, 1989; and others). Total reserves of magnesite are close to 2.5 million tons (Vakanjac and Tomanec, 1982).The Čajetina magnesite deposit is situated in the northeastern part of the Zlatibor ophiolite mountain complex, the ore field extending about 20 km^2. Ćave is one of the richest magnesite deposit located within the harzburgite and lherzolite host rocks, thrust onto Triassic limestones and a diabase-chert formation (mélange). The veins, varying in thickness from 0.1 to 1m, locally split into a stockwork arrangement of veinlets.

- The Kopaonik ore field comprises two contrasting ore types, the Trnava vein and stockwork deposit, and the sedimentary Bela Stena, interpreted as hydrothermal-exhalative (Raška, Kopaonik Mt.). Bela Stena is a bedded sedimentary deposit formed in the intermontane Neogene basin, situated within the Kopaonik ultramafic massif. It consists of either layers or lens-like (or lenticular) bodies, interstratified in the upper parts of the sedimentary sequence of the Jarandol Middle Miocene fresh-water basin (Ilić Jr., 1969b). This is the biggest magnesite sedimentary deposit in the Dinarides with 5.0 million tons of reserves. Chert, tuffs and subaquatic dacito-andesite, and boron minerals (colemanit, $Ca_2B_6O_{11}$; howlite, $Ca_2SiB_5O_9(OH)_5$, and elevated boron content in the sediments, point to a relationships between formation of magnesite and Tertiary volcanism (Ilić M. Sen., 1952; 1959).

- Trnava is a hydrothermal system of vein type I and type III, within the ultramafics, close to the zone of intensive Tertiary magmatism. The true hydrothermal vein systems hosted by ophiolites, and adjacent to the sedimentary ore, are supposed to be a feeder zone in the vast geothermal field, producing magnesite deposits of both types.

- Miličevci (Čačak) belongs to the same group of deposits.

- Goleš magnesite deposit, situated 15 km from Priština, Kosovo, belongs to vein type, group I and III (Fig. 4). It is located within the Goleš ultramafic massif built up of harzburgite, lherzolite, enstatite-dunite and serpentinite, covering an area of 15 km^2. The nearby fossil lateritic weathering crusts of Glavica, bears 7 million tons of Ni-laterites, presently mined as erosional remnants. This is the largest vein magnesite deposit in the Dinarides and the world, with total reserves close to 5 million tons. Most of the magnesite veins have a thickness of 0.5-3 m, while the biggest vein, Magura, is 20 m thick, 1200 m long, and 300 m deep. The magnesite is crypto-microcrystalline, white, locally slightly colored due to impurities (sesquioxides, R_2O_3, together with opal, chalcedony, quartz, sepiolite, serpentine, magnetite and limonite (Ilić Jr., 1969a; Ilić Jr. et al., 1995).

- Kamenica, (Beli Kamen, Kosovo) hydrothermal-sedimentary type, group VII, occurs in the Strezovac Tertiary basin, formed during Oligocene time between the Serbo-Macedonian massif on the east and the Vardar zone on the west, covering an area of 90 km^2. The basin is filled with volcano-sedimentary formations, siliceous reefs, siliciclastics, limestones, dolostones, pyroclastic and epiclastic sediments, interlayered with hydrothermal-sedimentary magnesite beds (Fig. 5; Ilić Jr. and Popević, 1970). The structure can be massive, layered or brecciated. The magnesite is white, or tint with yellow or gray hues. The total reserves of the ore field Beli Kamen is estimated to be of 3 million tons.

Tab. 2 - The thirteen new samples of cryptocrystalline magnesite deposits, sample locality, district, genetic type, coordinates and $\delta^{18}O$ and $\delta^{13}C$ values.

Sample	Locality	District	Genetic type	Symbol	X (°E)	Y (°N)	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)
M-1	Čajetina	Zlatibor	Infiltration (X)	□	19.74	43.78	-13.2	28.7
M-2	Kose	Zlatibor	Vein (I), stockwork (III)	○	19.75	43.58	-10.4	25.2
M-3	Krive Strane	Zlatibor	Vein (I), stockwork (III)	○	19.60	43.68	-13.1	26.5
M-4	Ćave	Zlatibor	Vein (I), stockwork (III)	○	19.60	43.66	-12.5	26.8
M-5	Mokra gora	Mokra gora	Infiltration (X)	□	19.53	43.83	-14.2	28.3
M-6	Kamenica	Kamenica	Hydrothermal-sedimentary (VII)	■	21.33	42.59	1.7	34.7
M-7	Bela Stena	Raška	Hydrothermal-sedimentary (VII)	■	20.62	43.38	1.2	35.0
M-8	Goleš 1	Goleš	Vein (I)	●	21.00	42.55	-13.5	26.0
M-9	Goleš 2	Goleš	Vein (I)	●	21.00	42.55	-13.8	27.7
M-10	Banovići	Konjuh	Vein-breccia (I)	●	18.54	44.41	-15.7	26.5
M-11	Banovići	Konjuh	Vein-breccia (I)	●	18.54	44.41	-14.8	26.8
M-12	Trnava	Raška	Vein (I)	●	20.53	43.31	-13.9	27.2
M-13	Milićevci	Čačak	Vein (I), stockwork (III)	○	20.33	43.99	-9.8	26.8

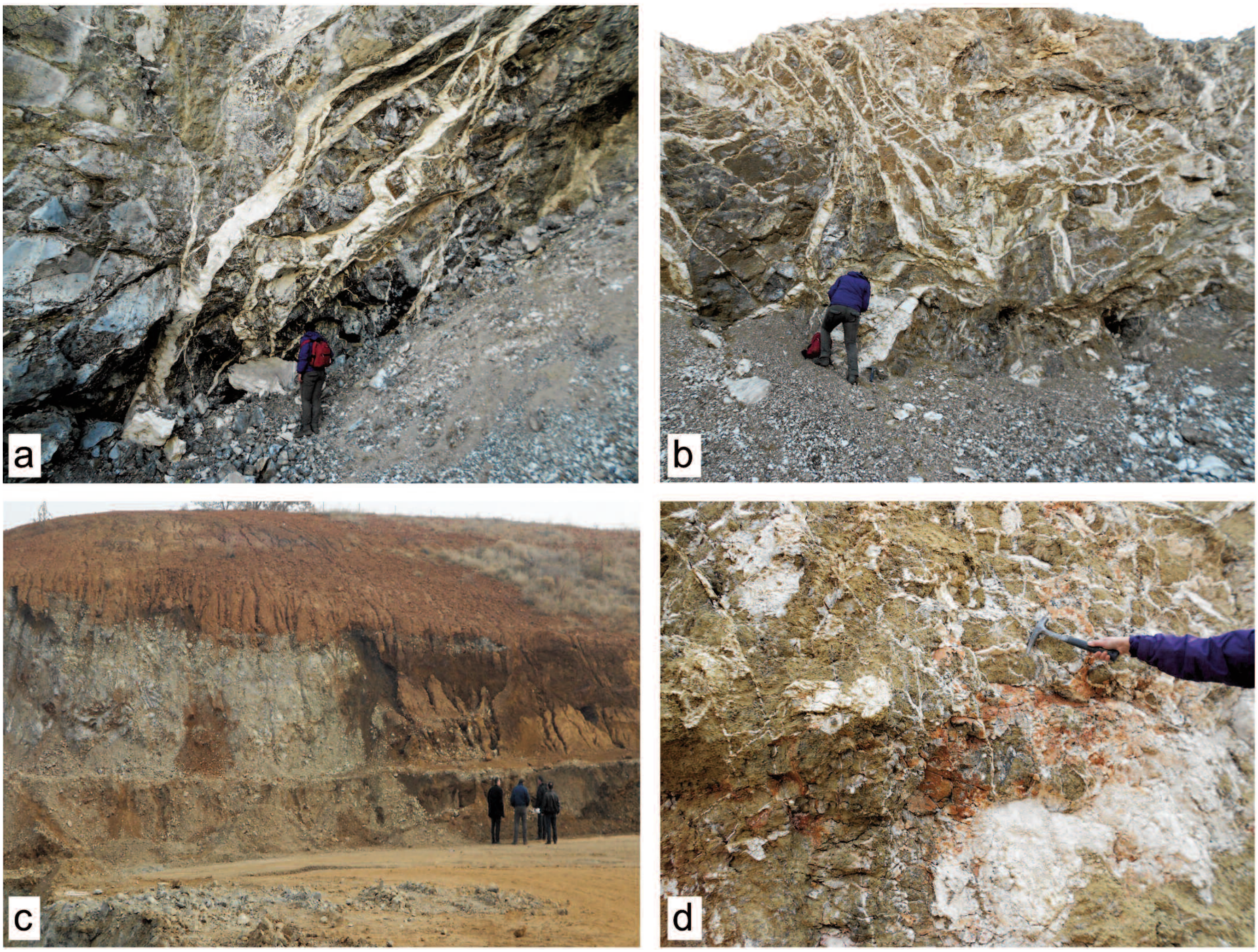

Fig. 4 - a and b) Goleš magnesite deposit, Kosovo, belongs to the vein type, group I. It is located on the Goleš ultramafic massif, built up of harzburgite, enstatite-dunite and serpentinite. This is the largest vein magnesite deposit in the Dinarides, and the world, with total reserves close to 5 mil. tons. c) Glavica fossil laterite crust, covering the Goleš ophiolites along their boundary as erosional remnants, occupies an area of 1 km^2. The laterite crust is 10-30 m thick, with 1.55% Ni, and 7.5 mil tons resources. d) Beneath the crust is a system of stockwork and vein type magnesite bodies, termed commonly as “infiltration” type.

Fig. 5 - Kamenica (Beli Kamen), Kosovo, hydrothermal-sedimentary magnesite formation deposited in the Strezovac basin between the Serbo-Macedonian massif on the east and the Vardar zone on the west, in Oligocene times.

- Mokra Gora deposit, is the infiltration type X, below the lateritic weathering crust. Late Cretaceous rudist limestones transgressively cover Triassic sediments, ophiolitic mélange and the thick lateritic crust over ophiolites. Below the thick layer of Ni-laterites and oolitic nickel-iron ore, a system of stockwork veins is consistent with an origin by infiltration, *per descendum* of the magnesite mineralization.

- The Banovići, 1 and 2 (Konjuh Mt.) mineralization belongs to vein-breccia type I. The samples were collected in the northernmost part of the Konjuh ophiolite complex. Banovići 1 represents a magnesite-serpentinite breccia zone, 3 to 10 m thick, while Banovići 2 is the mineralized breccia zone up to 8 m thick having the serpentinite as host rock. The paragenesis of ore minerals includes magnesite, with subordinate chalcedony, opal and sepiolite. Magnesite has microcrystalline texture (Sunarić-Pamić and Pamić, 1988).

ANALYTICAL METHODS

Carbon and oxygen isotope compositions were determined at the Stable Isotope Laboratory of the University of Lausanne, Switzerland by a Finnigan Mat Facility. Major and trace elements and rare earth elements (REE) were analysed by inductively coupled plasma mass spectrometry (ICP-MS) in the ACME Analytical Laboratories, Ltd, Vancouver, Canada, and by FUS-MS analysis method in the Activation Laboratory Ltd, Anchaster, Ontario, Canada. The results and detection limits are presented in Table 3.

RESULTS AND DISCUSSION

Genesis of cryptocrystalline magnesite deposits in the Dinarides has received controversial interpretations based on two major models. One (*per ascendum*) involves deposition of magnesite from hot ascending fluids, emanated by dehydration of either sedimentary or metamorphic rocks, or gravitated (artesian) meteoric water on the way up from the footwall of ophiolites. The other (*per descendum*) implies that meteoric waters, percolating down through fractures and fissures, leached the ophiolitic rocks and deposited magnesite by a process similar to the karstification of carbonates.

Per ascendum model

The isotopic data set, presented in Fig. 2, determined for the Dinaride cryptocrystalline magnesites, and confirmed by their counterparts in Turkey (Fallick et al., 1991; Zedef et al., 2000), show a positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values according to the equation:

$$\delta^{18}O = 0.508\ \delta^{13}C + 32.3$$

The correlation coefficient r = 0.904 is significant at the 99.9% level, for n = 42 measurements. Although supported by a limited number of measurements in this research (n = 13), the observed correlation $\delta^{18}O = 0.483\ \delta^{13}C + 33.4$, with r = 0.89, and a significance at 99.9% level, is approximately consistent with the former one.

Decarboxylation of organic matter and generation of isotopic light CO_2 requires $\delta^{18}O$ values of the order of -2‰ for water and is facilitated by temperatures around 70°C (Aharon, 1988). This geothermal regime is consistent with hydrostatic conditions of water circulating at 2-3 km depth, i.e., roughly corresponding to the thickness of the ophiolite thrust-sheets, to reach organic rich sediments overthrust by the ophiolites.

Precipitation of colloidal, crypto-microcrystalline magnesite and precipitation of dolomite and varieties of silica are triggered by pressure decrease and degassing of CO_2, when bicarbonate water approaches the surface. Fallick et al. (1991) and Zedef et al. (2000) consider the sudden release of carbon dioxide as the main mechanism for magnesite precipitation. Fallick et al. (1991), however, argue against devolatilization of CO_2 as a *raison d'ĕtre* for significant carbon isotope fractionation, because of the restricted span of isotope values among individual deposits, and the overall correlation between $\delta^{18}O$ and $\delta^{13}C$.

The Zlatibor magnesite, Čajetina, Kose, Krive Strane, Ćave magnesite consist of veins and ramifying veinlets. They plot in the $\delta^{13}C$-$\delta^{18}O$ restricted field of group I and III (Fig. 2), thus raising again the question of the existence of the infiltration type X as a separate group, rather than being consistent with the general model which controls the regression line.

The Mokra Gora magnesite, near the Zlatibor area, consists of closely spaced veinlets, and stockworks, locally covered by lateritic weathering crusts, classified as type X. The $\delta^{13}C$ is similar to those of th Goleš and Bakovići vein type (-13.2 to -14.2‰). The $\delta^{18}O$ is slightly higher (28.3 to 28.7‰) approaching values of the Ražana stockwork type III.

Bela Stena and Kamenica samples represent the second end member of the C-O isotope mixing line (Fallick et al., 1991). At the present knowledge, they are classified as sedimentary or hydrothermal-sedimentary deposits of type VII. The samples from the Bela Stena strata-bound deposit and the Kamenica, massive stratiform one, plot distinctly separated from the vein and stockwork deposits, at the highest values of $\delta^{18}O$ and $\delta^{13}C$, well fitting the general regression line (Bela Stena: $\delta^{18}O$ = 35.0‰, $\delta^{13}C$ = 1.2‰; Kamenica: $\delta^{18}O$ = 34.7‰, $\delta^{13}C$ = 1.7‰). These values strongly support a lacustrine sedimentary origin. The upper limit of the $\delta^{13}C$ value, which is close to +4‰ for the Bela Stena and Kamenica magnesite is readily explained by 9 to 10 per mil isotope enrichment from atmospheric CO_2 (-7‰). Their $\delta^{18}O$ (SMOW) in the range between 26.2 and 35.9 fall in the field of evaporated fresh water (ambient temperature and $\delta^{18}O$ values above SMOW).

The described models compare closely with those proposed by Fallick et al. (1991). The ascending model has been envisaged primarily to solve the problem of the very low

Tab. 3 - Major and trace elements for thirteen new magnesite samples.

Sample	Locality	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	MnO	LOI	Total	Ba	Sr	Th	U	Pb	Zn	Cu	Co	Ni	Cr	Y	Zr	Nb
		%	%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
M-1*	**Čajetina**	1.37	0.05	0.26	47.16	0.94	<0.01	<0.01	49.40	99.2	<1	1.3	0.05	0.03	<0.1	2	3.1	6.4	88.1	30	0.4	0.8	0.6
M-2**	**Kose**	0.05	0.01	0.03	47.32	1.15	<0.01	0.005	51.79	100.4	9	3.0	0.16	0.01	40	<30	<10	<1	20.0	<20	<0.5	5	<0.2
M-4**	**Čave**	0.54	0.12	0.28	46.64	1.12	0.07	0.006	51.71	100.5	22	2.0	0.10	0.02	<5	<30	<10	<1	<20	<20	<0.5	4	<0.2
M-5*	**Mokra gora**	10.11	0.12	1.42	41.72	1.86	<0.01	0.04	44.00	99.3	<1	3.7	<0.05	0.03	0.5	5	3.7	13.1	273.3	250	0.2	0.5	0.4
M-6*	**Kamenica**	5.05	<0.01	0.12	43.19	3.46	0.07	0.02	47.40	99.3	9	35.6	0.88	0.64	1.1	5	6.5	2.7	1.5	<10	1.1	1.5	0.5
M-7**	**Bela Stena**	1.53	0.27	0.17	45.93	1.38	0.08	0.008	51.09	100.5	14	63.0	0.36	0.93	<5	<30	<10	<1	<20	<20	<0.5	3	<0.2
M-8*	**Goleš 1**	8.02	0.05	0.05	44.43	0.53	0.02	0.004	47.54	100.7	3	2.0	<0.05	<0.01	0.5	3	5.1	2.8	17.1	<10	<0.1	0.4	0.4
M-9**	**Goleš 2**	1.46	<0.01	0.14	46.69	1.12	<0.01	0.04	49.80	99.2	4	<2	<0.05	0.01	<5	<30	<10	<1	80.0	<20	<0.5	1	<0.2
M-10*	**Banovići**	0.07	0.01	0.17	47.57	1.25	<0.01	0.01	50.20	99.2	2	4.6	<0.05	0.02	0.4	5	9.9	0.6	7.0	<10	<0.1	1.7	0.4
M-11*	**Banovići**	0.06	<0.01	0.24	46.04	2.62	<0.01	0.02	50.20	99.2	1	4.2	<0.05	0.01	0.7	3	3.4	1.6	13.0	<10	<0.1	0.5	0.4
M-12**	**Trnava**	0.03	<0.01	0.03	46.97	1.00	<0.01	<0.001	51.81	99.9	6	<2	<0.05	<0.01	<5	<30	<10	<1	<20	<20	<0.5	<1	<0.2
M-13**	**Milićevci**	3.69	0.02	0.29	43.97	4.08	<0.01	0.023	48.64	100.8	35	103.0	0.07	0.40	<5	<30	<10	3	100.0	50	<0.5	2	<0.2

* -ACME
** -ActLabs

$\delta^{13}C_{PDB}$ value in the vein-stockwork magnesite deposits by applying decarboxylation of organic matter as source of CO_2 in Triassic and/or Paleozoic sediments, lying two or three kilometres below the paleo-obduction-surface of the ultramafic bodies. The simplicity of the model solves the isotope problem, but raises the following serious questions that have to be taken into account by any objective interpretative protocol.

i)The significant regression line of isotope inter-dependence requires a steady decarboxylation process being active on a regional scale, from the Dinarides to Greece and Turkey, or elsewhere. Actually, to accept this model, we should admit the presence of a deep-seated, homogenous, organic-rich sedimentary source of CO_2, uniformly distributed below the obducted ophiolite nappes, at all stockwork-vein magnesite deposits. We might expect, however, great variability of C-isotope fractionation due to the full scale of aerobic and anaerobic degradation and maturation of buried organic matter.

ii) The vein system may extend laterally over some kilometers, but the veins pinch out at a depth of no more than a few hundred meters, mostly between 100 and 200 m (Goleš deposit, maximum depth is 300 m). This fact strongly undermines the possibility that the source of mineralizing fluid was sited at 2-3 km of depth.

iii) The proposed *per ascendum* model is not supported by relevant ore paragenesis in the veins. The deeply born fluid, loaded with bicarbonates with low pH, is supposed to dissolve serpentinites or serpentinized peridotites releasing Mg^{2+} by the reaction:

$$12H^+ + Mg_3Si_2O_5(OH)_4 = 3Mg^{2+} + 2H_4SiO_4 + 4H_2O$$

$$40H^+ + 10(Mg_{0.8}Fe_{0.2})_2SiO_4 + 3O_2 = 16Mg^{2+} + 2Fe_2O_3 + 10H_4SiO_4$$

The CO_2 provides hydrogen for their dissolution.

$$H_2O + CO_2 = H_2CO_3 = 2H^+ + CO_3^{2-}$$

Peridotites (harzburgite, dunite, lherzolite) contain, beside MgO, large amounts of FeO, about 7 wt% on average, in olivine, pyroxenes and spinel, and CaO, about 3.5 wt% on average, mainly in clinopyroxene (Coleman, 1977). During serpentinization, CaO is depleted down to 0.08 wt%, while silica is dissolved in the bicarbonate solution and precipitated nearby as opal, chalcedony and quartz. The great bulk of Fe, Mg and Ca coprecipitate as carbonates (ankerite, ferrodolomite, dolomite, calcite, magnesite, etc.) under favorable pH conditions. Silica-carbonate alteration rocks known in the literature as listvenites or listwanites are produced this way (Barnes et al., 1973; Spiridonov, 1991: Robinson et al., 2005). Listvenites are common alteration rocks in ophiolites, usually bearing mineralizations of mercury (Bailey, 1946; Everhart, 1950), polysulfides (Strmić-Palinkaš et al., 2007; Borojević-Šoštarić et al., 2011; Pamić and Olujić, 1974), stibnite and mercury (Maksimović, 1952; Maksimović and Brindley, 1980), gold (Likhoidov et al., 2007) etc., derived from the hydrothermal leaching of serpentinite and peridotite. The crypto-crystalline vein-stockwork magnesite bodies, however, are almost pure magnesium carbonate, with minor accessory chemical components and minerals from the serpentine and sepiolite group. They contain minor quantities of silica and dolomite in very thin alteration selvages, and are often in intimate contact with either fresh peridotite or serpentinite (Bodenlos, 1950; Sunarić-Pamić and Pamić, 1988; Dabitzias, 1980). The magnesite forming fluids must have been depleted in all elements, major, trace and REE, which accompany magnesium in the ultramafic precursor, requiring a self-refining process, similar to ion chromatography, characteristic in the laterite weathering crust.

iv) The CO_2 degassing mechanism needed for raising pH and thereby precipitating magnesite on the way to the surface, requires extremely high CO_2 fugacity, exceeding the hydrostatic pressure (Phyd = 25 bars) at the depth of 250 m. Such a high CO_2 fugacity should be supported by high total carbonate concentration of 13.5 g/l ($aH_2CO_3 + aHCO_3^- + aCO_3^{2-}$), at 75°C, and 41 g/l at 25°C (Perry et al., 1963; Rizhenko, 1963). The pH in the environment with inert channel walls would be close to 3 for both temperatures the H_2CO_3 being the major species in solution. However, ion HCO_3^- becomes dominant species by hydrolysis of magnesium silicates, which yields pH above 8, as testified on magnesium bicarbonate water within catchments and issues of spring waters exclusively in ophiolites from Cyprus, Greece, Northern Oman and Western USA (Barnes and O'Neil, 1971; Papastamataki, 1977; Neal and Stanger, 1994). Degassing CO_2 with PCO_2 of 25 bars, derived by decarboxylation, at higher pH, between 8 and 8.5, requires concentration of total carbonates between 58 and 160 g/l respectively, what is highly unrealistic.

A different interpretation of the "*per ascendum*" model has been given by Ilić Jr. (1969a). Magnesium is extracted by hydrothermal CO_2 rich fluids via lateral-secretion from the ophiolites beneath, followed by degassing and deposition of magnesite during upwelling to the paleo-surface. The vein deposits formed at low to medium hydrothermal temperatures during Miocene post-collisional regional magmatism. Ilić Jr. also recognized infiltration type magnesite deposits, below weathering crusts, representing a "shallow" phenomenon of minor importance, formed during Late Jurassic and Early Cretaceous time. Although reliable under some aspects, the model does not explain the origin of CO_{2-}, the persistent regression line of C and O isotopes, and the light carbon isotope composition of magnesite.

Some of the investigated deposits, Oshve, vein type II, and Mušiči-Greiner talc-breunerite, of type V (Table 1, Fig. 2), do not fit the mixing regression line, but cluster in separate groups at high C-isotope and low to intermediate O-isotope values. They can be interpreted by either the *per ascendum* or lateral-secretion models.

The Oshve magnesite vein is 450 m long, 0.5 to 10 m thick. The vein was confirmed down to a depth of 75 m by exploration drilling. It is located in the strongly serpentinized lherzolite, thrust on the Jurassic mélange, and cut by a shoshonite dyke. The vein has porculane texture, with local pisolotic appearance. It is roofed by highly silicified serpentinite, impregnated by cauliflower magnesite, in the ten meter thick silica cap (Fig. 6a, b) representing a spring of hydrothermal water. Sunarić-Pamić and Pamić (1988) explained the deviation of isotope values in the Oshve type deposits as evidence of hydrothermal activity related to numerous shoshonitic and andesitic dykes (31 Ma) in the central part of the zone (Fig. 2). High value of C-isotopes might be attributed to magmatic origin or possible thermal decarbonization of Triassic carbonate rocks beneath (Fallick et al., 1991). Pohl (1990) argued for an epigenetic hydrothermal origin of the Kraubath type magnesite, characterized by moderate temperature and low salinity, degassing CO_2, eventually boiling, self sealing and erupting.

The Mušić-Greiner breunerite magnesite vein system occurs sideways of a huge chrysotile-asbestos deposit, at the locality of Bosansko Petrovo Selo (Ozren Mt.; Vakanjac, 1964). Intrusion of an albite-rhyolite body produced a 70 m wide metasomatic-hydrothermal halo made of the following zones: granitoid - quartz-carbonates - talc - serpentinite - carbonate (listvenite, rodingite). Magnesite veins (with accessory siderite) crosscut serpentinized lherzolite and asbestos veins as the latest hydrothermal event (Fig. 7a, b). Carbon isotopes have high values possibly indicating the same origin proposed for the Oshve deposit (Fig. 2). The higher values of O-isotopes might be a result of addition of meteoric water and subsequent decrease of temperature.

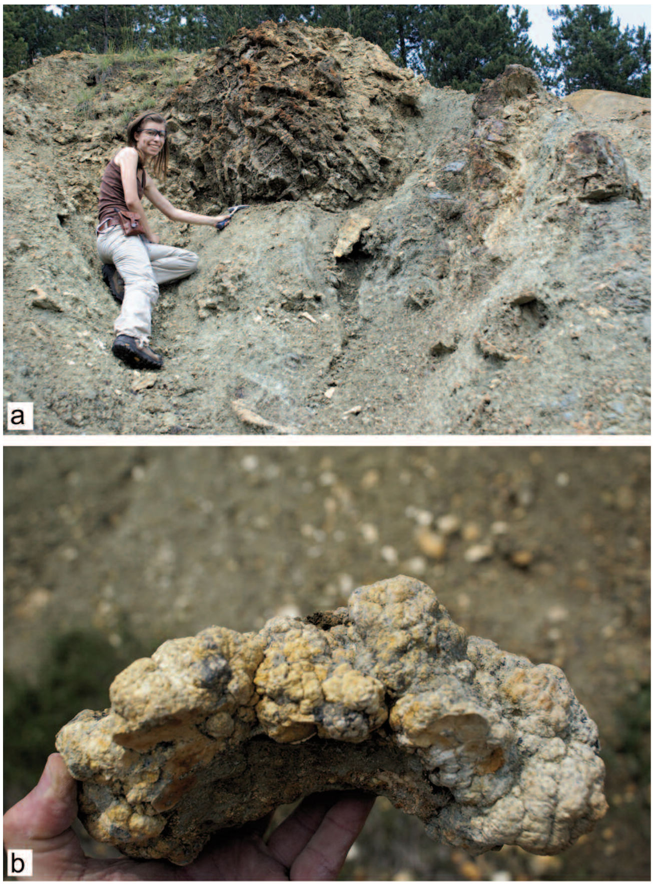

Fig. 6 - a and b) The Oshve magnesite vein system in the strongly serpentinized lherzolite, thrust on the Jurassic mélange, and cut by a shoshonite dyke. A porculane texture of the magnesite veins, at places assumes pisolitic appearance. High values of C-isotopes are attributed to either a magmatic origin or possible thermal decarbonization of Triassic carbonate rocks underneath.

Per descendum model

The "*per descendum*" model, with ore forming fluid percolating from the surface, down through a laterite weathering crust, provides physical and chemical conditions necessary for the formation of vein-stockwork magnesite deposits (Petrov, 1967; Petrov et al., 1979; Lapčević, 1988).

The release of magnesium starts in the lateritic weathering crust. The process involves agglomeration of effectively adsorbent hydroxide colloids and smectites, acting as a true chromatographic column. The major elements are distributed through the vertical topographic profile according to their respective mobilities (Trescases, 1973). Fe, Cr, Ti, and Al, occurring as hydrolyzates (goethite, little gibbsite) or residual minerals (chromite, magnetite) are the most immobile elements, concentrated in the uppermost layer of the weathering crust. Co and Mn, precipitate as hydroxide concretion, in the middle part of the crust. Ni is distributed all over the profile with clear tendency to concentrate in the

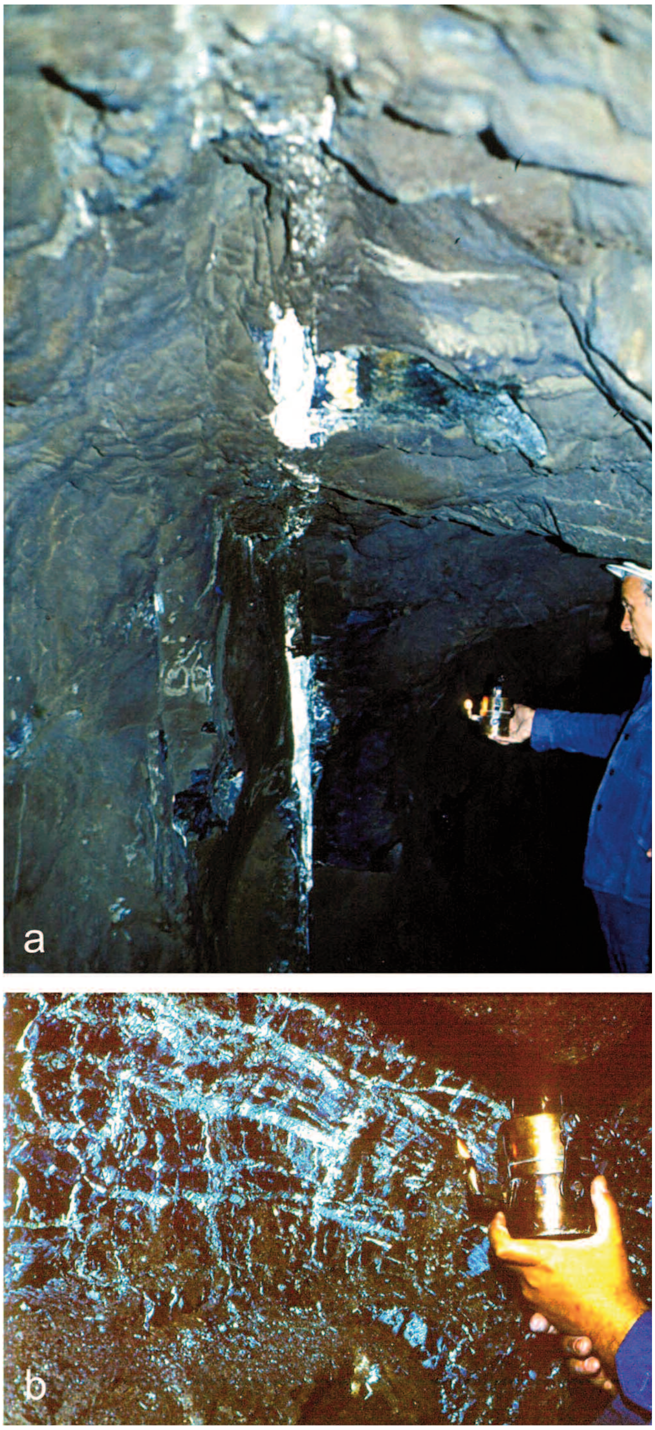

Fig. 7 - a and b) The Mušić-Greiner breunerite magnesite vein system is sideway of a huge chrysotile-asbestos deposit, Bosansko Petrovo Selo (Ozren Mt.). Magnesite veins (with accessory siderite) crosscut serpentinized lherzolite and asbestos veins as the latest hydrothermal formation.

newly formed ferruginous silicates. Silica fixation or removal depend on the position of the temporary water table, forming smectites or even silcretes. Magnesium and calcium migrate downwards, eventually precipitating by increasing pH of percolating water in the saprolite. Deeper penetration, underneath fresh ophiolitic ultramafic rock, depends on local morphological and tectonic conditions. The well drained area consisted of high grounds of highly fractured, obducted ultramafics, underlain by effective aquifers made of a diabase-chert formation, and Triassic carbonates are the most favorable for the formation of magnesite (Milivojević, 1996; Komatina and Čubrilović, 1996).

In more detail, percolating Mg-HCO_3 groundwater loaded with atmospheric CO_2 represents a partially/effectively "closed" system. The free CO_2 phase controls pH. The primary minerals of the host rocks are subjected to low temperature serpentinization, which consumes H^+ ions. If CO_2 is not any more freely available in the conduit, progressive consumption of CO_2 causes the pH to raise, enhancing magnesite precipitation and increasing the Ca/Mg ratio. Water is chemically modified into a Ca-OH type and superalkaline solution with pH up to 11-12. Evolution of Mg-HCO_3 water into Ca-OH type has been documented in the Cyprus ophiolitic complex, Oman, Semail ophiolite, New Caledonia, and California, (Barnes et al., 1978; Neal and Shand, 2002), Bosnia Kulaši, (Derković, 1973) and Serbia, Mokra Gora, (Milovanović, 2011). Weathering crusts played an important role as barriers for those elements which accompany magnesium in the ophiolitic protolith, preventing their co-precipitation with magnesite, as a complex mixture of ferroan carbonates, as in listvanites.

Thermal effects necessary to explain low $\delta^{18}O$ values (between 27.7 and 26.5‰) in vein magnesite are created by exothermic reactions, serpentinization, hydration of primary silicates and precipitation of magnesite, without involving deep circulation of water in a high geothermal regime. Numerous thermal springs surround the Zlatibor ophiolite complex (Milivojević, 1996), suggesting current exothermic serpentinization underground.

The O- and C-isotopic evidence

Remarkable persistence of the isotope regression lines for magnesite deposits of the Dinarides, of Turkey, Greece, and elsewhere, strongly supports a global process for magnesite formation (O'Neil and Barnes, 1971; Gartzos, 1990; Fallick et al. 1991; Zedef et al., 2000; Horkel et al., 2009).

Magnesite deposits associated with volcanic and/or igneous-driven hydrothermal-metasomatism such as those at Oshve, type II, and Mušići, Greiner talc-breunnerite type V, obviously fall out of the regression line, being special genetic types.

The extremely low values of carbon isotopes observed in some magnesite veins, however, could be explained by an alternative model not involving mixing with isotopic light CO_2 derived from decarboxylation of organic matter (HODC).

A side effect of limited CO_2 supply, due to lack of exchange with the atmosphere and intensive sequestration of CO_2 by magnesite precipitation, stops atmospheric CO_2 (or mixture with those from soil, $\delta^{13}C$ -10 to -24 per mil) to mediate the isotopic composition of precipitating magnesite. Under these circumstances, the isotopic composition of precipitating magnesite is exclusively controlled by fractionation of carbon isotopes between magnesite and predominant HCO_3^{2-} species in the solution on the way down, following the Rayleigh equation:

$$\delta^{13}C_{HCO3^-} = [(\delta^{13}C_{HCO3-,I}) + 1000]\, f(\alpha - 1) - 1000$$

$\delta^{13}C_{HCO3,I}$ is the initial isotope composition of the HCO_3^- species, dominant in the pH range between 6.3-10.3, in contact with atmospheric or soil $CO_{2(g)}$; $\delta^{13}C_{HCO3}$ is the isotope composition of HCO_3^- after deposition of magnesite in solution isolated from atmospheric $CO_{2(g)}$; f is the fraction of HCO_3^- remaining, and α is the fractionation factor $R_{magnesite\ (dolomite)}/R_{HCO3-}$. All α values for carbon isotopes among CO_2(g), HCO_3^-, and dolomite were used as approximations for $MgCO_3$, because of the lack of appropriate reference data for magnesite. Variation of initial isotope values of $CO_{2(g)}$ (-7 to -23 per mil), and temperature dependence of between 25 and 70°C (Emrich et al., 1970) gave a full scale of decreasing isotope values of vein-magnesite up to -16 per mil. The model assumes for simplicity, a "closed" system with atmospheric-soil CO_2 avoided from magnesite deposition in veins and stockworks. In reality, however, one may except certain prolongation of atmospheric-soil CO_2 influence during the *per descendum* percolation of groundwater.

The trace elements evidence

There have been many attempts to use trace elements as a tool to distinguish the infiltration-*per-descendum* from the hydrothermal-circulation-*per-ascendum* models for generation of magnesite deposits via alteration of ultramafic rocks.

The exceedingly low REE contents of cryptocrystalline vein and sedimentary magnesite deposits testifies that Mg^{2+} is derived from ultramafics, extremely poor in rare earth elements (Morteani et al., 1982; 1983).

The magnesite deposits investigated in this work are incorporated into two prominent ophiolite belts, the Dinaride and Vardar ones (Karamata et al., 1980). These belts are distinguished by a broad criterion based on predominance of lherzolite and harzburgite mantle rocks (Janković, 1990; Pamić and Jurković, 1997; Jurković, 2000; 2001). Peridotites from mantle suites, in general, have "concave" chondrite normalized geochemistry pattern (V-shaped) and very low REE (0.06-0.6 x chondrite) (Fig. 8, Table 4) as determined on the Semail ophiolites (Coleman, 1977; Pallister and Knight, 1981). Furthermore, the patterns appear to remain undisturbed after intensive serpentinization, exceeding 60-85%, testifying to the high immobility of REE. The data on REE in the Dinaride ophiolites are scarce, limited to those reported by Šegvić (2009) for the Konjuh-Krivaja lherzolite complex and Slovenec (2003) for the harzburgite of Medvednica Mt. (Western Vardar ophiolite zone) (Fig. 9). The chondrite normalized patterns of the investigated magnesites show peculiarities of the REE patterns easily recognizable as inherited from the ophiolitic precursors, either harzburgite or lherzolite. The most apparent examples are the Goleš vein deposits 1 and 2, where the REE chondrite-normalized distribution literally mimics the pattern of peridotites showing the typical "concave" trend (Fig. 8). Mirroring of a precursor REE pattern is the effect of total complexation as Ln-dicarbonate ions across the REE suite due to a steady increase of pH, reaching a value of 9 (Bau and Möller, 1992; Johannesson and Hendry, 2000).

Similarity with the REE chondritic pattern of peridotites is observed in the hydrothermal-sedimentary deposit of Kamenica (Fig. 8), accounted for by its location in the Vardar zone with predominant harzburgite rocks. Magnesite forming fluids in Kamenica were venting through the Oligocene lake sediments, however, the REE pattern still suggests a harzburgite source, although the trace elements testify to a contribution of sedimentary rocks (sialic elements), especially the Ba, Sr, Th, U, and extremely low Ni contents (Fig. 10).

The Bela Stena sedimentary deposit shows a drastically different REE pattern (Fig. 9) compared with Kamenica. The trend is rather flat, resembling greatly the REE chondrite-normalized patterns of shales, a clear evidence of the two contrasting genetic models, hydrothermal-sedimentary, for Kamenica and sedimentary for Bela Stena, respectively.

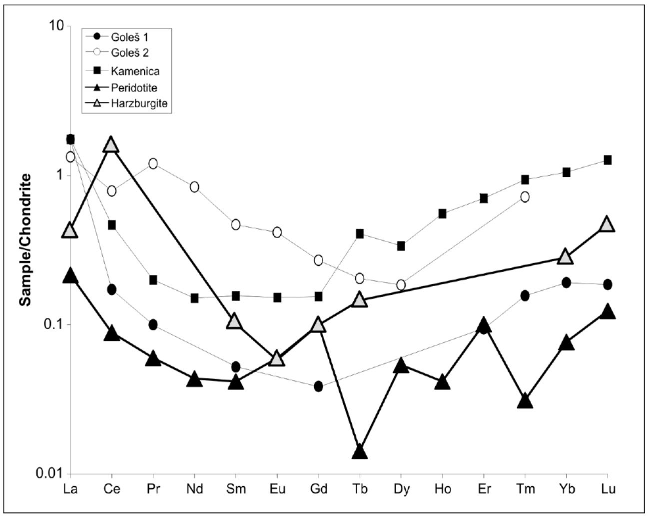

Fig. 8 - Chondrite normalized patterns (Hanson, 1980) of magnesite samples from the "harzburgite" belt. Goleš 1 and Goleš 2 and Kamenica, literally mimic characteristic patterns of the average peridotite taken from Coleman (1977) and of harzburgite from Pallister and Knight (1981).

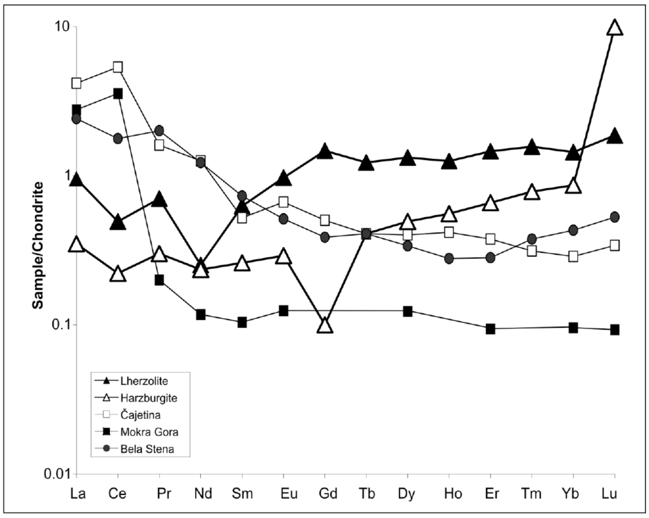

Fig. 9 - Chondrite normalized patterns (Hanson, 1980) of magnesite samples from the "lherzolite" belt are partly inherited from the host rock, (composition of lherzolite taken from Šegvić, 2009, and harzburgite from Slovenec, 2003).

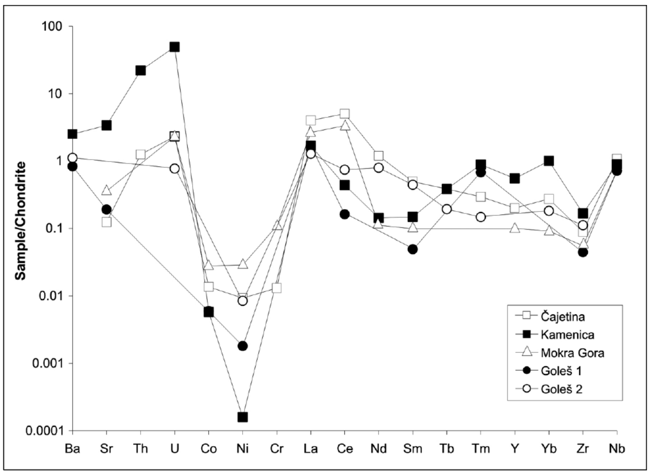

Fig. 10 - Spider diagram normalized to primordial mantle marks two processes, i) contribution of sedimentary rocks (sialic elements) in the Kamenica sample and, ii) steady decrease of Ni and Co, as well as of the Ni/Co ratio, suggesting variable degrees of weathering in the overlying lateritic crust.

Tab. 4 - REE in thirteen magnesite samples, REE in ultramafic rocks are refered from lherzolite, Konjuh-Krivaja ophiolitic complex, Bosnia, (Šegvić, 2009); harzburgite, Medvednica Mt., Croatia, (Slovenec, 2003), and average peridotite (Coleman, 1977).

Sample	Locality	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	La/Lu	La/Gd	Lu/Gd	Ce/Ce*	Eu/Eu*
		ppm																			
M-1*	Čajetina	1.31	4.34	0.16	0.75	0.10	0.048	0.13	0.02	0.13	0.03	0.08	0.010	0.06	0.011	16.58	12.2	8.3	0.7	2.1	1.3
M-2**	Kose	0.44	0.83	0.12	0.45	0.15	0.036	0.08	0.01	0.06	0.01	0.03	0.008	0.06	0.010	7.48	4.5	4.5	1.0	0.8	1.0
M-4**	Ćave	0.50	0.98	0.17	0.63	0.14	0.039	0.10	0.01	0.07	0.01	0.04	0.009	0.07	0.012	8.94	4.3	4.1	1.0	0.7	1.0
M-5*	Mokra gora	0.87	2.89	0.02	0.07	0.02	0.009	<0.01	<0.01	0.04	<0.01	0.02	<0.005	0.02	0.003	7.27	29.7	-	-	4.8	-
M-6*	Kamenica	0.55	0.38	0.02	0.09	0.03	0.011	0.04	0.02	0.11	0.04	0.15	0.030	0.22	0.041	8.29	1.4	11.3	8.2	0.8	1.0
M-7**	Bela Stena	0.76	1.44	0.20	0.73	0.14	0.037	0.10	0.02	0.11	0.02	0.06	0.012	0.09	0.017	11.67	4.6	6.3	1.4	0.8	1.0
M-8*	Goleš	0.55	0.14	0.01	<0.05	0.01	<0.005	0.01	<0.01	<0.01	<0.01	<0.01	0.023	<0.01	<0.002	2.83	-	45.2	0.0	0.4	-
M-9**	Goleš	0.42	0.64	0.12	0.50	0.09	0.030	0.07	0.01	0.06	<0.01	0.02	0.005	0.04	0.006	6.33	7.2	4.9	0.7	0.6	1.2
M-10*	Banovići	0.69	1.17	0.02	0.17	<0.01	<0.005	<0.01	<0.01	<0.01	<0.01	<0.01	<0.005	0.01	<0.002	4.16	-	-	-	2.2	-
M-11*	Banovići	0.70	0.7	0.03	0.07	0.01	<0.005	0.01	<0.01	0.02	<0.01	0.01	<0.005	0.02	<0.002	3.80	-	57.6	0.0	1.1	-
M-12**	Trnava	0.27	0.48	0.08	0.32	0.08	0.018	0.05	<0.01	0.03	<0.01	0.02	<0.005	0.03	0.004	4.10	6.9	4.4	0.6	0.7	0.9
M-13**	Milićevci	0.43	0.87	0.13	0.54	0.11	0.036	0.09	<0.01	0.04	<0.01	0.03	0.007	0.06	0.008	7.08	5.5	3.9	0.7	0.8	1.1
Lherzolite[1]	Konjuh	0.30	0.40	0.07	0.15	0.12	0.070	0.38	0.06	0.43	0.09	0.31	0.050	0.3	0.060						
Harzburgite[2]	Medvednica	0.11	0.18	0.03	0.14	0.05	0.021	0.08	0.02	0.16	0.04	0.14	0.025	0.18	0.320						
Average peridotite[3]		0.068	0.072	0.006	0.026	0.008	0.0043	0.0125	0.0007	0.0175	0.003	0.0215	0.0010	0.016	0.0040						
Chondrite[4]		0.315	0.813	0.100	0.597	0.192	0.0722	0.2590	0.0490	0.3250	0.072	0.2130	0.0320	0.209	0.0323						

[1] Šegvić (2009); [2] Slovenec (2003); [3] Coleman (1977); [4] Henson (1980)
* -ACME
** -ActLabs

Fluid inclusion study on collemanite crystals in the borate rich layer at the Piskanje locality (Bela Stena ore district), 3.5-4.5 m thick, with collemanite, howlite, nobleite, jarandolite, ulexite, probetite, tuzlaite, hydroboracite, studenitsite, stronginorite, and veatchite, evidences $NaCl-CaCl_2-H_2O$ fluids with high bulk salinity of 6.6-12.9% NaCl equ. (Szabó et al., 2009). It suggests a playa-lake evaporitic environment of the Jarandol Miocene lacustrine basin (Helvaci, 2005).

The Bela Stena and Kamenica deposits could be compared with Salda Gölü, western Turkey, and Hirsizdere in the middle of the Büjük Menderes graben (Zedef et al., 2000). The Salda Gölü is a recent evaporitic lake, filled with meteoric water driven by topographic gradient through an ultramafic coarse alluvium. Hydromagnesite microbiolites are diagenetical equivalents of the ancient lacustrine deposit of Bela Stena.

An example of Hirsizdere deposit, embedded within Pliocene lacustrine sediments, corresponds to the Kamenica magnesites, a counterpart with augmented C-isotope ratio controlled by atmospheric carbon dioxide and formed at relatively higher temperature (≤ 100°C) by deposition from thermal waters (Zedef et al., 2000).

The magnesite deposits of Trnava on the Kopaonik Mt. (Vardar ophiolite zone), the Čajetina, Ćave, and Kose deposits on Zlatibor Mt. and the Banovići 2 in the Konjuh-Krivaja ophiolite (Dinaridic ophiolite belt), occur in ophiolites with predominant lherzolite (Pamić and Jurković, 1997). The chondrite normalized patterns of magnesite from Čajetina and Mokra Gora (Fig. 9) are characterized by high LREE/HREE and La/Lu ratios, 12.2 and 29.7, respectively, and the highest positive Ce anomalies, of 2.1 and 4.8, respectively (Table 4). The explanation for these features can be found in the lateritic processes that occurred above the magnesite veins.

The released rare-earth elements, by disintegration of Mg-silicates of serpentinized peridotite in a saprolite zone, are concentrated in clay-rich and iron-bearing colloids of the lateritic horizon (Lottermoser, 1989). The moderate pH 6-7 in the saprolite zone enables the highest fractionation of REE. LREE are predominantly as Ln^{3+} elemental and carbonate species $Ln(CO_3)^+$ forms, while HREE are efficiently complexed forming hydroxides and carbonates $Ln(OH)^o$ and $Ln(CO_3)_2^-$. Their fixation in the lateritic profile is controlled by a different mechanism. Positive ions are concentrated in iron colloids and smectites, while negative or neutral complexes are gradually impoverished raising the La/Lu ratio (Henderson, 1996; Johannesson and Hendry, 2000). Ce^{4+} is fixed by co-precipitation with iron hydroxide. The lateritization process terminates with formation of a ferruginous crust, with very low pH, and leaching of all elements including REE. The mobilized REE descending down by percolating water keep changing their REE pattern developed in the particular horizons of the laterite zone. Lanthanide patterns indicate that these elements were primarily accumulated in the uppermost ferruginous crust and then remobilized and discriminately deposited in the underlying horizons (Dequincey et al., 2002).

CONCLUSION

The research has been focused on the genesis of cryptocrystalline vein-stockwork magnesite deposits in the Dinaric ophiolites. Thirteen samples from the magnesite deposits of the Dinaric and Vardar ophiolite belts were analyzed for C- and O-isotopes, trace elements and REE, to shed more light on the origin of different types of magnesite deposits occurring along the entire Tethyan ophiolite belt, from the Alps to Zagros Mountains. Between the two controversial genetic models involving opposite direction of flow of the ore forming fluids *per ascendum* and *per descendum*, the authors favour the latter. Among the various arguments in favour and against each model, the following are the most significant.

Variation of stable isotope ratio $\delta^{18}O$ vs. $\delta^{13}C$ in the various magnesite deposits define a unique shape of regression line that requires uniform conditions of formation, on a regional scale. Supply of light CO_2, needed for gaining low C-isotope values in the vein magnesite proposed by the "*per ascendum*" model, would have implied that organic-rich sediments undergoing decarboxylation occurred uniformly at a depth of 2-3 km beneath the entire ophiolite belt, that is not the case.

The "*per descendum*" model offers an alternative explanation involving evolution of C-isotopes from heavy to light by gradual precipitation of the heavier C-isotope in magnesite, while the light ones are progressively enriched in the descending fluid. The closed or semi-closed system regarding CO_2 supply in the fluid from the lateritic weathering crusts downward is controlled by the Rayleigh equation. It does not require exceptionally light $\delta^{13}CO_2$ and satisfies the model with the CO_2 of atmospheric or soil origin having an initial value between -7‰ and -23‰.

Extremely low concentrations of REE and trace elements, as well as simple monomineralic parageneses, are results of precipitation of a "clean descending fluid" already purified by weathering processes in the thick lateritic crust. In contrast, "*per ascendum*" hydrothermal fluids, mobilizing all the elements present in the peridotite precursor by lateral-secretion would produce complex ferroan carbonate parageneses, approaching mineral assemblages typical of listvenites.

Degassing as a cause for magnesite precipitation in the veins reaching 300 m of depth requires high partial pressure of the CO_2 free phase, and extremely unrealistic high concentrations of total CO_2 under high pH conditions.

$Mg-HCO_3$ waters leaving a lateritic crust gradually precipitate magnesite on the way down, controlled by increasing pH, leading to generation of magnesium poor water of Ca-OH type as the final product. Magnesitization is a phenomenon similar to karstification in many respects.

REE chondrite-normalized patterns in magnesites reflect processes in the weathering lateritic crust. Mobilization of REE in saprolite by carbonate complexing, fixation and fractionation of LREE and HREE in the lateritic zone by adsorption on colloids and clays, and remobilization of REE in the ferruginous crust, control the shape of the final patterns in the magnesite vein-stockwork system beneath.

The most likely time for lateritization and magnesitization is Early Cretaceous time, but for the real hydrothermal deposits, the hydrothermal-sedimentary and sedimentary ones is Miocene, a time of collisional-post-collisional magmatism across the Inner Dinarides and Vardar zone. The authors accept the possibility that thermal effects of Neogene magmatism might have generated hydrothermal cells creating more complex fluid circulation at certain localities.

The new analytical data provided in this work bring further support to the "*per decendum*" model, which is already accepted by many researchers as a widespread phenomenon leading to the formation of magnesite deposits in ophiolitic terrains.

The future research has to be focused on well exposed outcrops, the best in operating mines, with sampling in systematic manner from the top to the bottom of the veins, and has to include a fluid inclusion study.

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