

## MINERALOGY OF MAGNESITE FROM THE PČINJA RIVER AREA – NORTH MACEDONIA

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**A b s t r a c t:** Magnesite from the Pčinja river area most often occurs in the form of veins of varying thickness and length, with their orientation being determined by the direction of faults and cracks. In certain parts of the terrain, the appearance of multiple subparallel veins is observed, while in other places they cross, branch, or locally disappear and reappear. It appears as microcrystalline mass resembling unglazed porcelain. Its fracture is conchoidal, the hardness is 3½ – 4½, its streak is white and the density is 3.0–3.2 g/cm<sup>3</sup>. Based on the XRD pattern magnesite is the dominant crystalline phase. The unit cell parameters obtained using the main reflection lines of X-ray diffraction are:  $a = b = 4.63 \pm 0.002 \text{ \AA}$ ,  $c = 15.02 \pm 0.003 \text{ \AA}$ ,  $V = 279.35 \text{ \AA}^3$ . In addition to magnesite, the presence of serpentine, dolomite and talc has also been determined. The absence of a pronounced basal reflection near 12° indicates that serpentine is not the dominant phase. Dolomite fits into the genesis as an indicator of the early phase of carbonization, and this is genetically very significant. During the initial carbonization of serpentinite, CO<sub>2</sub>-rich fluids react with serpentine which also contains Ca (taken from pyroxenes). While Ca is still available in the system, Ca-Mg carbonate is formed dolomite. This occurs at relatively higher temperatures (~350°C). When Ca is depleted from the system (excreted by fluids), reactions continue only with Mg pure magnesite is formed. At the same time, Si released from the serpentine reacts with Mg and water to give talc. This occurs at lower temperatures (~280°C). The dolomite in the examined samples indicates that carbonization has proceeded quite far. Most of it has already been converted to magnesite, and only a small relict amount remains. The serpentine is present but nearly consumed. The Pčinja river area represents an advanced stage of carbonization, where CO<sub>2</sub>-rich hydrothermal fluids have converted ~85–90% of the original serpentinite to magnesite, with only isolated relict patches of serpentine surviving. This is entirely consistent with Type I cryptocrystalline magnesite deposits of the Balkan ophiolitic belt.

**Key words:** magnesite; serpentine; ultrabasic rocks; Pčinja river

### 1. INTRODUCTION

The occurrences of magnesite in the area of the confluence of the Pčinja river into the Vardar river are located in the central ophiolite belt of the Vardar zone, which in this part is basically represented by ultrabasic rocks of the harzburgite and dunite types (Božović et al., 2013; Boev and Lepitkova, 2002). The term ophiolite first appeared in 1813 and was interpreted as a serpentinized peridotite associated with a group of igneous rocks that evolved exclusively on the ocean floor, in the mid-ocean ridges (MOR) (Prelević et al., 2014; Gass, 1975; Moores

and Vine, 1971; Coleman, 1977). Later this definition was questioned by Miyashiro (1973). Based on geochemical investigations of the Troodos ophiolite complex (Cyprus), the close spatial and temporal occurrence of MOR-basalts with igneous rocks that typically show a calc-alkaline trend related to subduction was recognized. Although the magmatic origin of ophiolites in mid-ocean ridges is undoubted (Dilek and Furnes, 2011, 2014) divided ophiolites into suprasubduction zone, continental margin, mid-ocean ridge, plume-type, volcanic arc and accretionary-type ophiolites.

Magnesite belongs to the group of carbonate minerals with the chemical formula  $\text{MgCO}_3$ . It has great economic importance and is used primarily for the industrial production of refractory materials that have applications in metallurgy (Canterford, 2007; Wang et al., 2011; Hussein, 2018). It also produces various chemical compounds based on magnesium, which are then used to solve certain environmental problems, including the extraction of carbon dioxide (Kelemen and Matter, 2008). The formation of magnesite is a complex geological process, especially for magnesite that occurs within ultrabasic rocks (serpentinites, dunites, harzburgites) (Peretti et al., 1992). Magnesite is formed in the interaction of solutions rich in  $\text{CO}_2$  and magnesium present in ultrabasic rocks (Beinlich et al., 2020). The mineral magnesite itself is characterized by a crystalline structure that in most cases varies from fine-grained to coarse-grained depending on the conditions of formation. Based on the genesis of formation, as well as the geological conditions in which it occurs, magnesite can be divided into two basic groups or basic types, namely: magnesite, which most often occurs in association with ultrabasic rocks, which is cryptocrystalline; and layered magnesite, which occurs in association with marine carbonate sediments, usually within marine platforms (Fallick et al., 1991; Zedef et al., 2000; Pohl, 1989, 1990, 2011; Abu-Jaber and Kimberley, 1992; Jurković et al., 2012).

The process of formation of magnesite, i.e. genesis, is closely related to the processes of serpentinization that occur within ultrabasic rocks (peridotites), where in the processes of hydrothermal alterations (hydration) the formation of serpentine minerals (antigorite, chrysotile, lizardite, and others) occurs. In this process, the enrichment of ultrabasic rocks with magnesium occurs, whereby magnesite itself is deposited along tectonic structures (veins and veinlets) (Kahya and Kuşçu, 2016; Obeso et al., 2022; Gartzos, 1986.). However, it must be mentioned that magnesite does not occur in all serpentinized ultrabasic massifs, but only in those in which solutions rich in  $\text{CO}_2$  appear during the serpentinization processes themselves. The study of the isotopic composition of magnesite can provide good insight into the conditions of its formation. Variations in the stable isotopes of carbon and oxygen can largely explain the conditions that were present in the hydrothermal solutions and the conditions of the environment in which the magnesites were deposited

(Zedef et al., 2000; Schroll, 2002; Gartzos, 1986, 2004; Jedrysek and Halas, 1990).

### *Local geology*

The wider environment of the magnesite deposit in the area of the confluence of the Pčinja river into the Vardar river is characterized by a complex geological structure, formed as a result of long-term and multi-phase geotectonic evolution. This area hosts rock complexes of different ages, lithological composition and genetic origin, among which sedimentary, magmatic and metamorphic members are distinguished. Their mutual spatial connection, as well as the pronounced tectonic disturbance of the terrain, were of essential importance for the formation, localization and preservation of magnesite deposits.

Magnesites in the Pčinja river area occur within the ultrabasic rocks that are part of the local geology of this area. The geology of this area itself (Figure 1) includes the following geological formations:

1. Alluvium, which occurs along the course of the Pčinja river and is mainly made up of fragments of rocks (limestones, harzburgites, amphibolites, clay minerals), which have varying dimensions.
2. Amphibolites and amphibolite schists, as part of the metamorphic complex of the Vardar zone, green rocks that appear as bands in the geological structure of the terrain.
3. Quartz sandstones and conglomerates, which appear as a transgressive series through older geological formations (Paleozoic, Jurassic, and Cretaceous), are composed of sandstones and conglomerates with heterogeneous geological composition.
4. Diabase hornblende formation (of Triassic-Jurassic age), which in the present is represented by rocks of the quartzite group, as well as ultrabasic rocks (diabases, gabbros).
5. Massive limestones of Triassic age, represented by dark gray bands of limestone rocks.
6. Pliocene sediments, which have a heterogeneous lithological structure (sandstones, clays).
7. Serpentinites as part of the ultrabasic complex of the Vardar zone.
8. Flysch zone, represented by platy sandstones and clays.
9. Cretaceous limestones, that appear in the contact areas with ultrabasic rocks, gray-white with a crystalline structure.

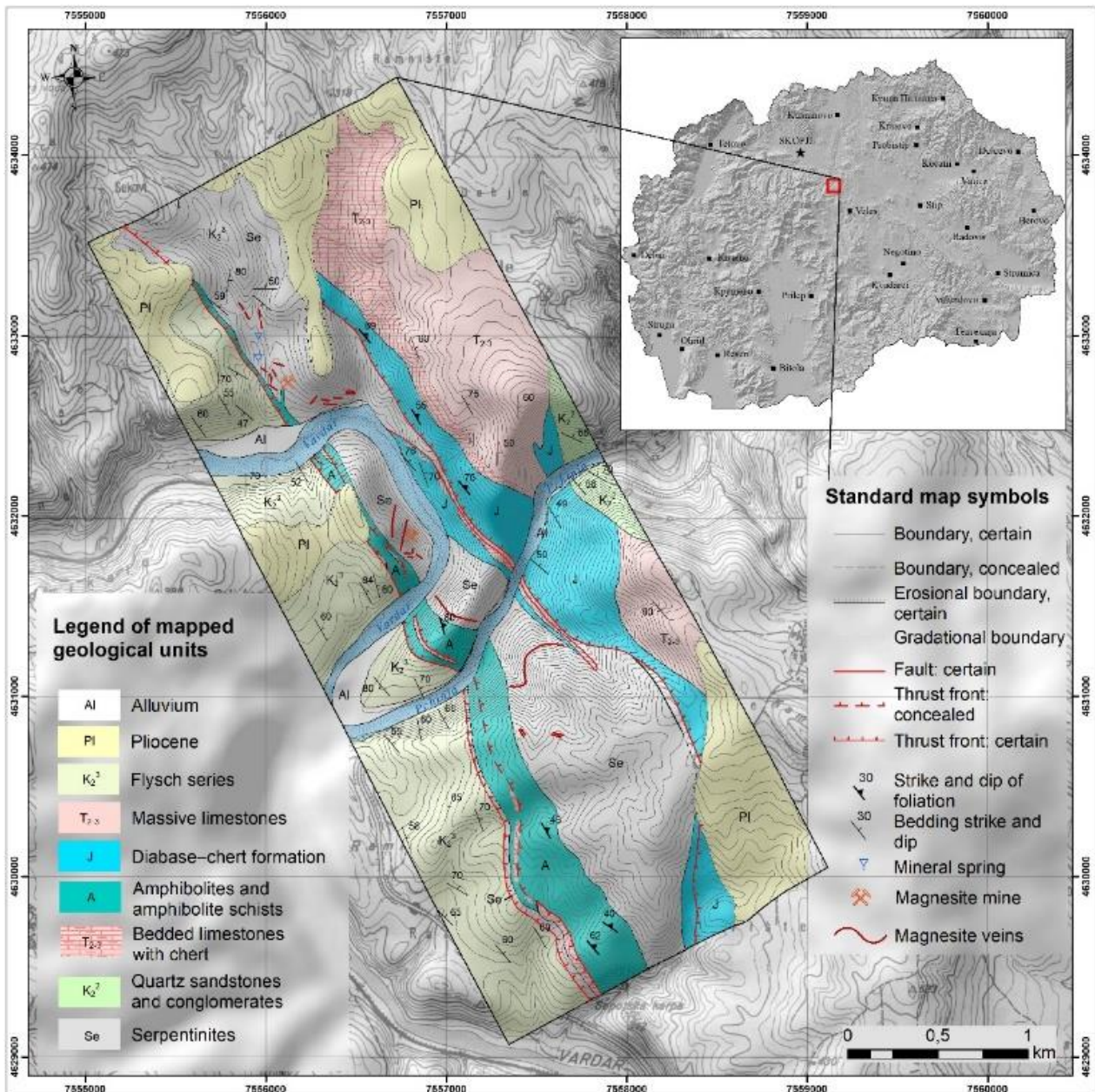


Fig. 1. Geological map of the Pčinja river area (map prepared by Andov

### Description of the occurrence of magnesite

The magnesites from the Pčinja river confluence into the Vardar river occur within the ultrabasic complex of the Vardar zone. Here, the ultrabasic rocks are represented by dunites and harzburgites (Figure 2). Microscopic examinations of the harzburgites, which are more widely distributed in this area, have a granular structure and are basically made up of olivine (which is completely converted into serpentine), pyroxene, and magnetite and chromite appear as accessory minerals (Figures 3 and 4).

Serpentinites occupy the central part of the area where magnesite veins appear (Figure 5). They are the product of serpentinization of ultrabasic rocks (harzburgites and dunites), that have undergone significant mineralogical and structural changes under the influence of tectonic movements and hydrothermal processes. A pronounced heterogeneity is observed within the serpentinite mass, where the rock is compact and massive in some places, while in others it is strongly fractured, mylonitized and tectonically fragmented.

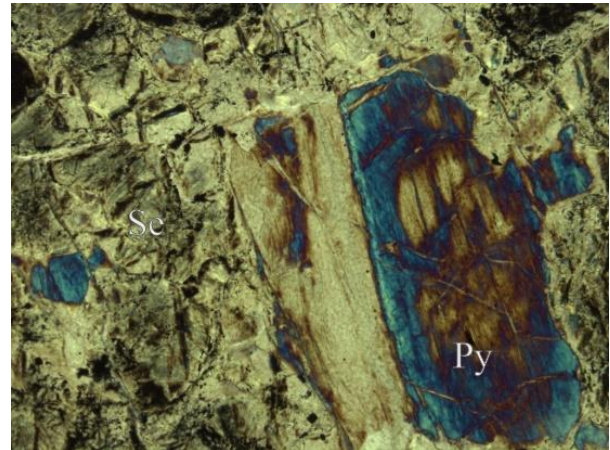
In the immediate vicinity of the serpentinites, amphibolites and amphibole schists also occur,

which represent metamorphic members with significance for contact relations and the general geological evolution of the area.

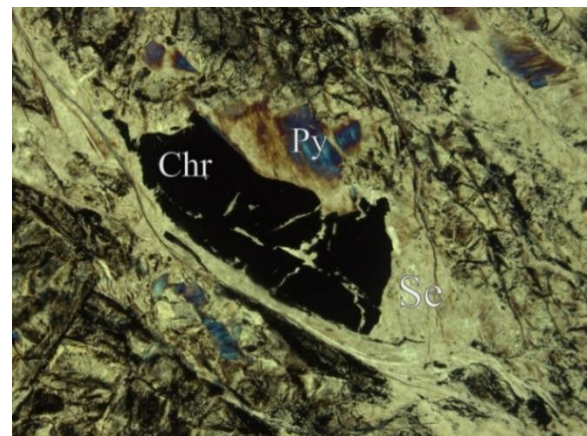
Magnesite most often occurs in the form of veins of varying thickness and length, whose orientation is controlled by the direction of faults and cracks. In certain parts of the terrain, the appearance of multiple subparallel veins is observed, while in other places they cross, branch or locally disappear and reappear. At the contacts between some magnesite veins and serpentinites, sepiolite and opal also occur.



**Fig. 2.** Ultrabasic rock from the vicinity of the Pčinja river area (photo I. Boev)



**Fig. 3.** Microscopic photograph of harzburgite from the Pčinja river area (serpentine, pyroxene), crossed nichols (Magnif.  $\times 100$ )



**Fig. 4.** Microscopic photograph of harzburgite from the Pčinja river area (serpentine, pyroxene chromite), crossed nichols (Magnif.  $\times 100$ )



**Fig. 5.** Magnesite wire in serpentine base (photo I. Boev)

## METHODOLOGY

To ensure a reliable characterization of the mineral species in this study, the following analytical methods were used: Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS), ICP-MS, and X-ray Powder Diffraction (XRPD).

*Scanning electron microscopy SEM-EDS.* – Analyses and electron micrographs were obtained using a VEGA3 LMU scanning electron microscope, with magnifications up to  $2 \times 1,000,000$ . Semi-quantitative chemical analyses were performed using appropriate standards, as listed below: O: SiO<sub>2</sub>; Na: Albite; Mg: MgO; Al: Al<sub>2</sub>O<sub>3</sub>; Si: SiO<sub>2</sub>; P: GaP; Ca: wollastonite; Ti: Ti; Fe: Fe; Br: KBr. Prior to analysis, the samples were sputter-coated with a thin layer of gold to ensure surface conductivity for both SEM imaging and EDS analysis.

*ICP-MS.* – This method provides a rapid and precise means of monitoring up to 50 elements simultaneously for minor and trace levels. The ICP-MS.

technique is widely recommended as a versatile analytical method for multi-element analyses. The sample solution is introduced into the system and is ionized through an introductory nebulizer. The plasma (ionized argon) produces temperatures close to 7.000°C, which thermally excites the outer-shell electrons of the elements in the sample.

*X-ray powder diffraction (XRPD).* – Analyses were carried out by conventional X-ray diffraction (XRD) techniques on bulk samples. For the present analysis, X-ray diffraction system (Shimadzu) diffractometer, series XRD 6100, with Cu (1.54060 Å) radiation operating at 40 kV and 30 mA. The powdered sample was scanned over the 5 – 80° range with step size of 0.02° and scanning speed of 1.2°/min. The analyzed material then is finely ground, homogenized, and average bulk composition is determined using the corresponding diagrams from Match, version 4.

## RESULTS AND DISCUSSION

Magnesite is magnesium carbonate with the formula MgCO<sub>3</sub> and belongs to calcite group minerals. It appears as microcrystalline mass resembling unglazed porcelain (Figure 6). Its fracture is conchoidal, hardness is 3.5–4.5, streak is white, and its density is 3.0–3.2 g/cm<sup>3</sup>.



Fig. 6. Macroscopic features on magnesite from the Pčinja river area

### Sample 1

Figures 7a,b,c,d show a fine-grained and relatively homogenous matrix. Grains are irregular in

shape and partially aggregated. No well-developed crystal faces indicate a massive or microcrystalline texture. The SEM/EDS analyses indicate that the sample consists of: dominant Mg-C-O phase (magnesite) which appears in massive/compact grains and secondary Mg-Si-O phase (serpentine) which appears in finer, lamellar/unstructured areas.

### Sample 2

The images in Figures 8a,b show two different textures: left side very homogeneous, fine “smooth” matrix with unclear crystal structure. This is most often: amorphous or microcrystalline phase or very fine-grained material. Right side (where Spectrum 13 and 14 are) plate/lamellar structure looks like: “sheets” or “packets”. This is typical of carbonates-magnesite. SEM-EDS analysis indicates a Mg-rich carbonate phase (magnesite) with minor (0.2%) Ni-bearing signature, suggesting secondary carbonization of serpentinized ultramafic material. The presence of Ni + Fe + Si traces strongly suggests this magnesite formed in an ultramafic geological setting (serpentine/ophiolite), which is the most common natural origin for magnesite deposits – consistent with the findings of: Zedef et al. (2000); Wicks and O'Hanley (1988); Corre et al. (2023).

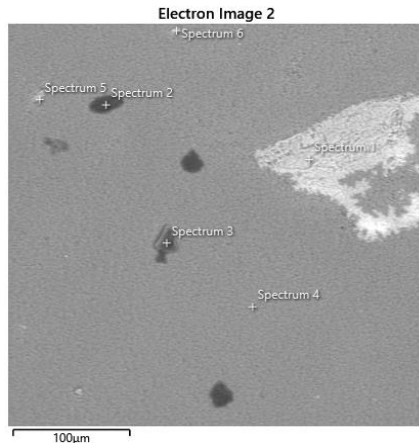


Fig. 7a. SEM image of sample 1

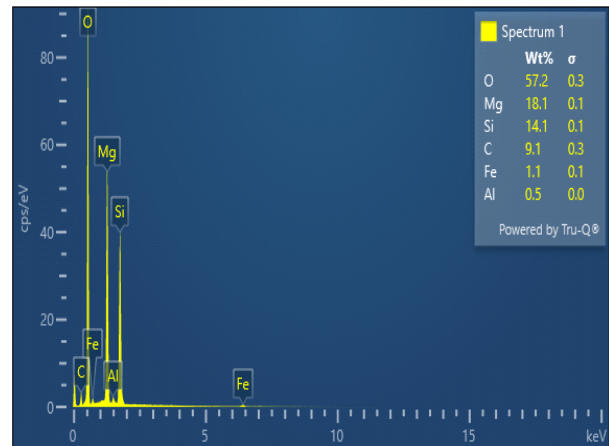


Fig. 7b. EDX of serpentine

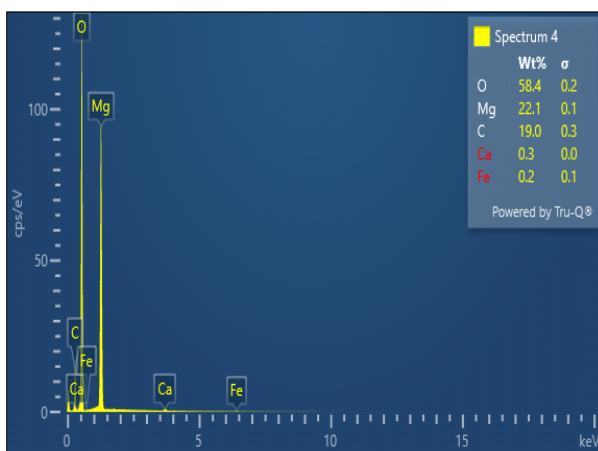


Fig. 7c. EDX of magnesite

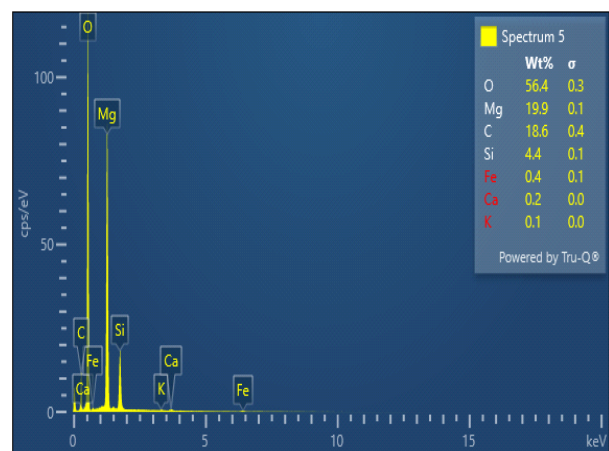


Fig. 7d. EDX of magnesite+serpentine

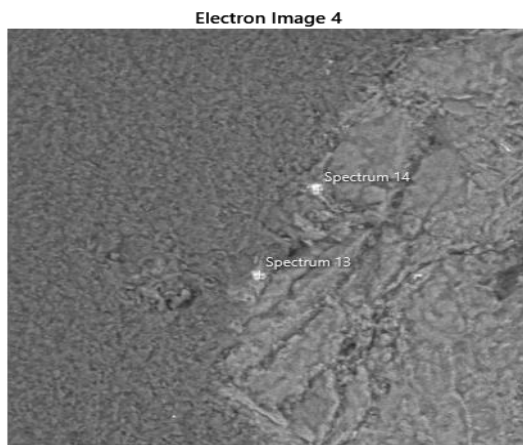


Fig. 8a. SEM image of sample 2

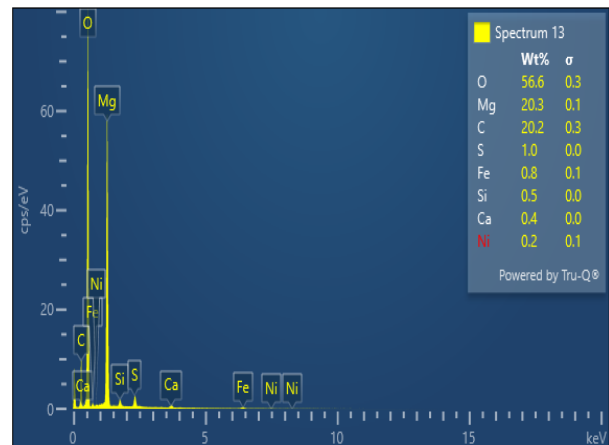


Fig. 8b. EDX of magnesite

### Sample 3

Figure 9a shows a fine-grained and relatively homogenous matrix. Grains are: irregular in shape and partially aggregated. No well-developed crystal faces indicates a massive or microcrystalline texture. The SEM/EDS analyses (Figures 9b,c,d) indicate that the sample consists of: dominant Mg-C-O

phase (magnesite), which appears in massive/compact grains, and secondary Mg-Si-O phase (serpentine), which appears in finer, lamellar/unstructured areas.

Figures 10 show that the main grain is irregular and sub-rounded. It has no sharp crystal edges-non-euhedral morphology, which indicates on secondary formation (alteration product). These three spectra

together provide a complete snapshot of the carbonation reaction from relic serpentine (spectrum 7) through the active replacement front (spectrum 10) to fully formed magnesite (spectrum 12), a remarkable preservation of the magnesite formation mechanism in the Pčinja river area, Vardar zone, north Macedonia. The serpentine is present, but nearly consumed. The Pčinja river area represents an advanced stage of carbonation where CO<sub>2</sub>-rich hydrothermal fluids have converted ~85–90% of the

original serpentine to magnesite, with only isolated relic patches of serpentine surviving. This is entirely consistent with Type I cryptocrystalline magnesite deposits of the Balkan ophiolitic belt.

XRPD did not show serpentine because serpentine is a poorly crystallized mineral. Its peaks at 12° and 24° may be broad and weak, easily lost in background. Also, if present in small amounts, XRPD may not detect it above the detection threshold (~3–5%).

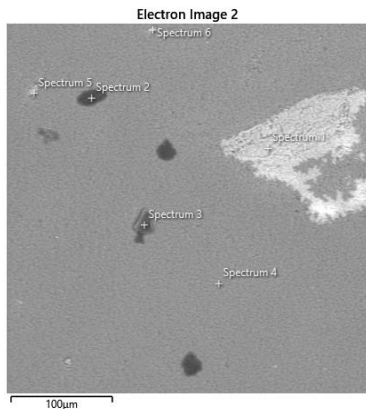


Fig. 9a. SEM image of serpentine and magnesite

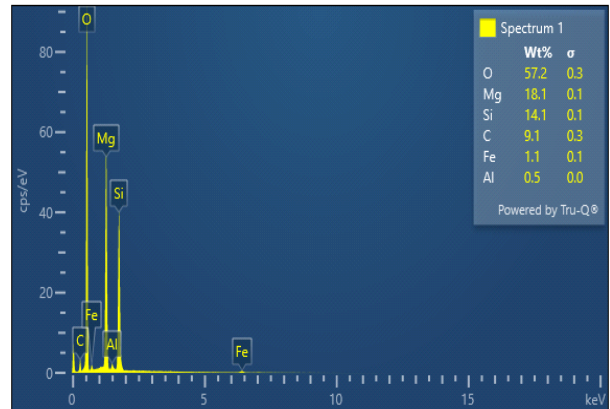


Fig. 9b. EDX of serpentine

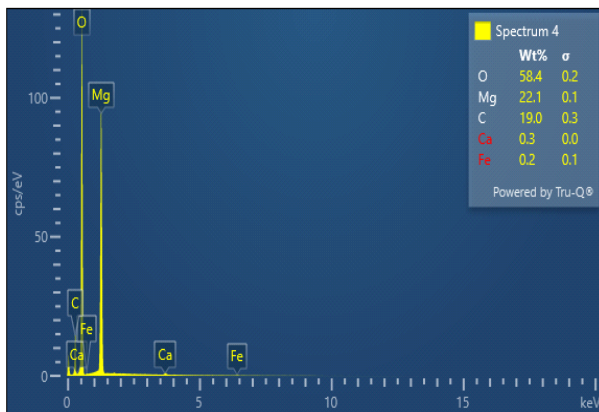
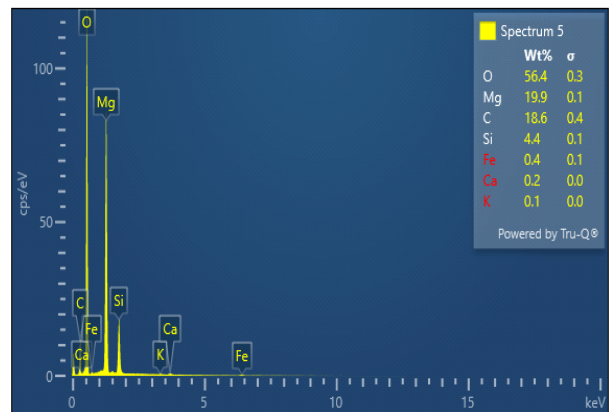


Fig. 9c. EDX of magnesite



Fvig. 9d. d) EDX of serpentine

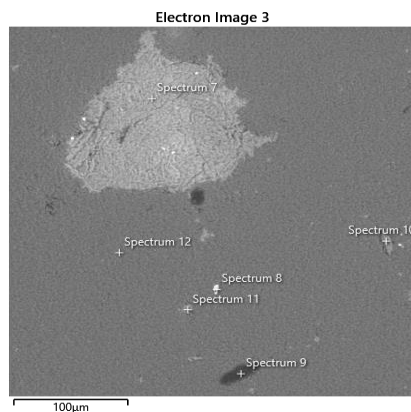


Fig. 10a. SEM image of magnesite and serpentine

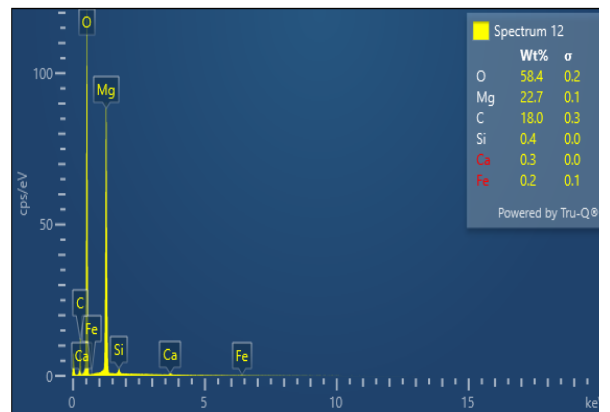


Fig. 10b. EDX of magnesite

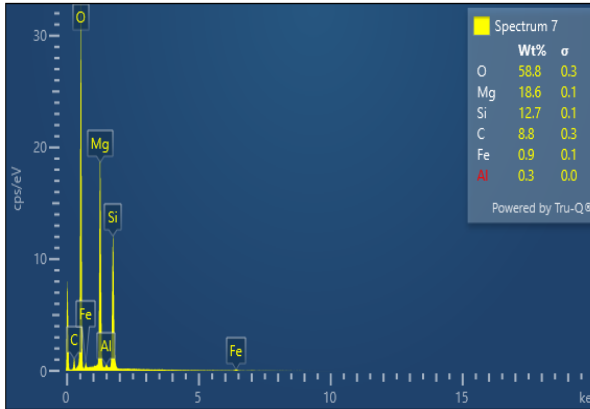


Fig. 10c. EDX of serpentine

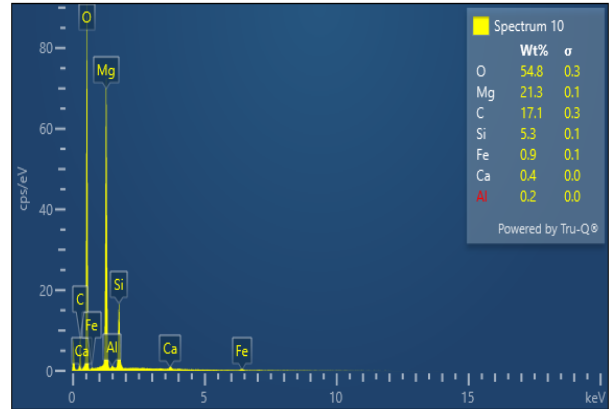


Fig. 10d. EDX of magnesite+serpentine

Sample 4

Figures 11 show that the sample consists of a highly agglomerated structure of fine particles. Particles are irregular and sub-rounded. Mostly sub-microns to a few microns. No well-defined crystal face indicates a secondary-alteration mineral phase.

EDX diagrams show minor Fe substitutions and Ca impurities.

Figures 12 show that on the left side has fine grained compact matrix. On the right side around (spectrum 22) has flake-like structure laured aggregates. In the center are present flatter-rounded grains.

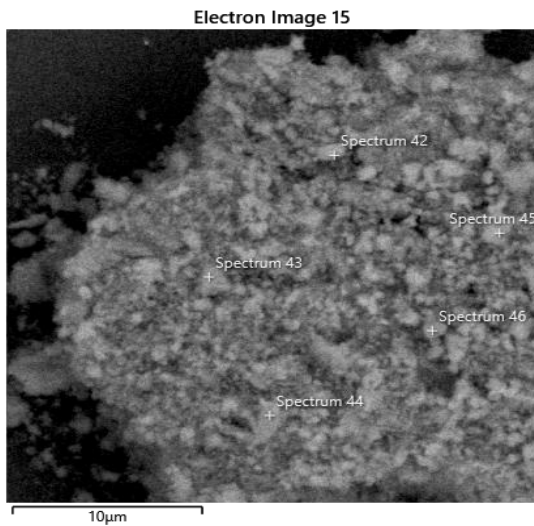


Fig. 11a. SEM image of magnesite

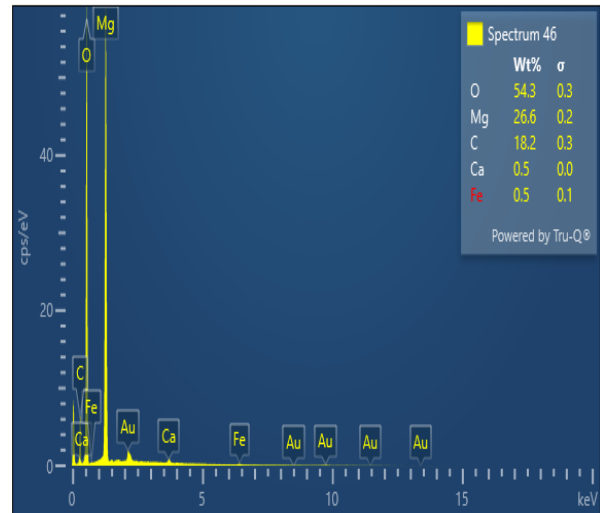


Fig. 11b. EDX of magnesite

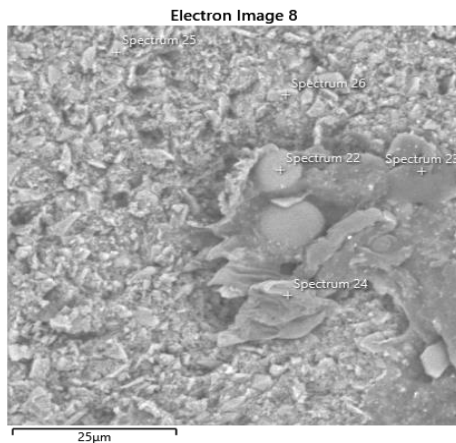


Fig. 12a. SEM image of talc

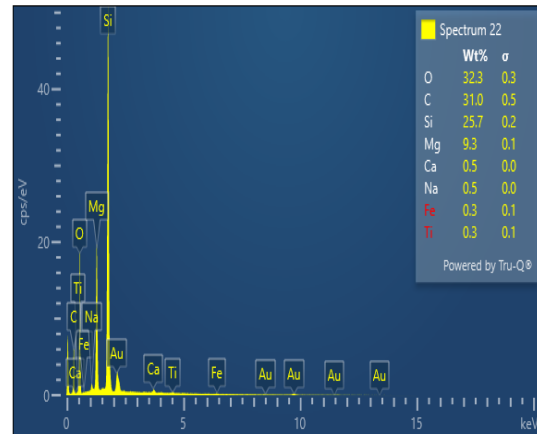


Fig. 12b. EDX of talc

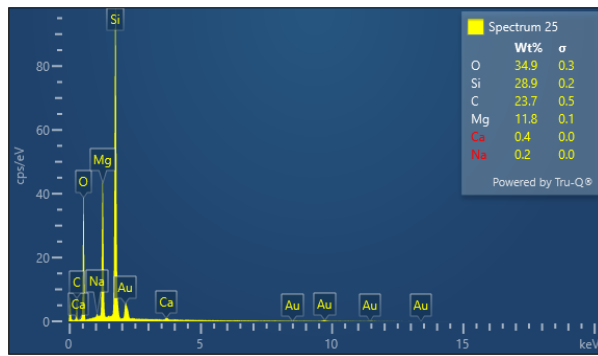


Fig. 12c. EDX of talc

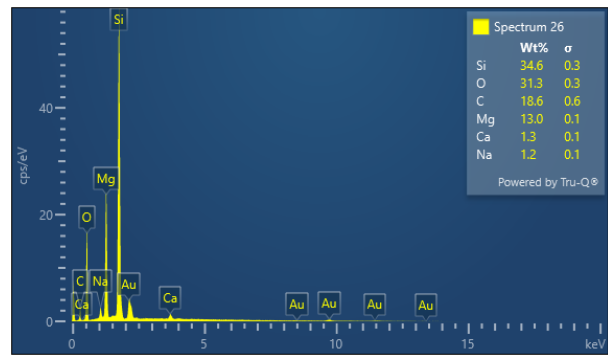


Fig. 12d. EDX of talc

From Table 1 it can be seen that the contents of Co is 2.5–4.0%, Ni 33.8–37.9%, Zn 1.6–4.3%, Sr <1.4%, Pd <1.7, Cs 1.0–1.2, Li 0.1–0.3, B 1.0–2.5, Cr 2.1–3.7 %. All other elements are below <0.1%. All samples show low but consistent FeO typical of ophiolitic magnesite.

Table 1

Chemical composition of magnesite from the Pčinja river area (major and trace elements) (%)

Oxides	Sample 1	Sample 2	Sample 3	Sample 4
Na <sub>2</sub> O	0.001	0.003	0.002	0.002
MgO	21.662	25.807	30.031	25.399
Al <sub>2</sub> O <sub>3</sub>	0.011	0.012	0.029	0.015
SiO <sub>2</sub>	0.004	0.0034	0.010	0.003
K <sub>2</sub> O	0.002	0.003	0.004	0.004
CaO	0.812	0.566	0.693	1.944
MnO	0.024	0.027	0.012	0.028
FeO	0.166	0.191	0.105	0.188
Elements	mg/kg	mg/kg	mg/kg	mg/kg
Co	3.2	4.0	2.5	4.0
Ni	29.1	35.8	37.9	33.8
Cu	<1	<1	<1	<1
Zn	4.3	3.3	1.6	1.7
Ga	<1	<1	<1	<1
Ge	<1	<1	<1	<1
As	<1	<1	<1	<1
Se	<1	<1	<1	<1
Rb	<1	<1	<1	<1
Sr	<1	<1	<1	1.4
Mo	<1	<1	<1	<1
Pd	<1	1.7	<1	<1
Ag	<1	<1	<1	<1
Cd	<1	<1	<1	<1
Sn	<1	<1	<1	<1
Sb	<1	<1	<1	<1
Cs	1.0	1.2	1.2	1.2
Ba	<1	<1	<1	<1
Tl	<1	<1	<1	<1
Pb	<1	<1	<1	<1
Bi	<1	<1	<1	<1
Li	0.2	0.2	0.3	0.1
Be	<1	<1	<1	<1
B	1.0	2.5	<1	<1
Ti	<1	<1	<1	<1
V	<1	<1	<1	<1
Cr	2.1	2.1	<1	3.7

From Table 2 it can be seen that the content of U is 0.104 to 0.206, Y 0.206 to 0.282; Ce to 0,132, Sc to 0.180 mg/kg. All other elements are <0.1 mg/kg.

Table 2

Chemical composition of magnesite from the Pčinja river area (rare earths elements) (mg/kg)

Elements	Sample 1	Sample 2	Sample 3	Sample 4
Sc	<0.1	<0.1	0.180	<0.1
Y	0.282	0.242	<0.1	0.271
Nb	<0.1	<0.1	<0.1	<0.1
In	<0.1	<0.1	<0.1	<0.1
Te	<0.1	<0.1	<0.1	<0.1
La	<0.1	<0.1	<0.1	<0.1
Ce	<0.1	0.132	<0.1	<0.1
Pr	<0.1	<0.1	<0.1	<0.1
Nd	<0.1	<0.1	<0.1	<0.1
Sm	<0.1	<0.1	<0.1	<0.1
Eu	<0.1	<0.1	<0.1	<0.1
Gd	<0.1	<0.1	<0.1	<0.1
Tb	<0.1	<0.1	<0.1	<0.1
Dy	<0.1	<0.1	<0.1	<0.1
Ho	<0.1	<0.1	<0.1	<0.1
Er	<0.1	<0.1	<0.1	<0.1
Tm	<0.1	<0.1	<0.1	<0.1
Yb	<0.1	<0.1	<0.1	<0.1
Lu	<0.1	<0.1	<0.1	<0.1
Hf	<0.1	<0.1	<0.1	<0.1
Ta	<0.1	<0.1	<0.1	<0.1
W	<0.1	<0.1	<0.1	<0.1
Os	<0.1	<0.1	<0.1	<0.1
Th	<0.1	<0.1	<0.1	<0.1
U	0.206	0.106	0.110	0.104

XRPD patterns on investigated samples are given in Figure 13. The most intense registered maxima in the studied powder pattern area compared with the corresponding maxima of magnesite.

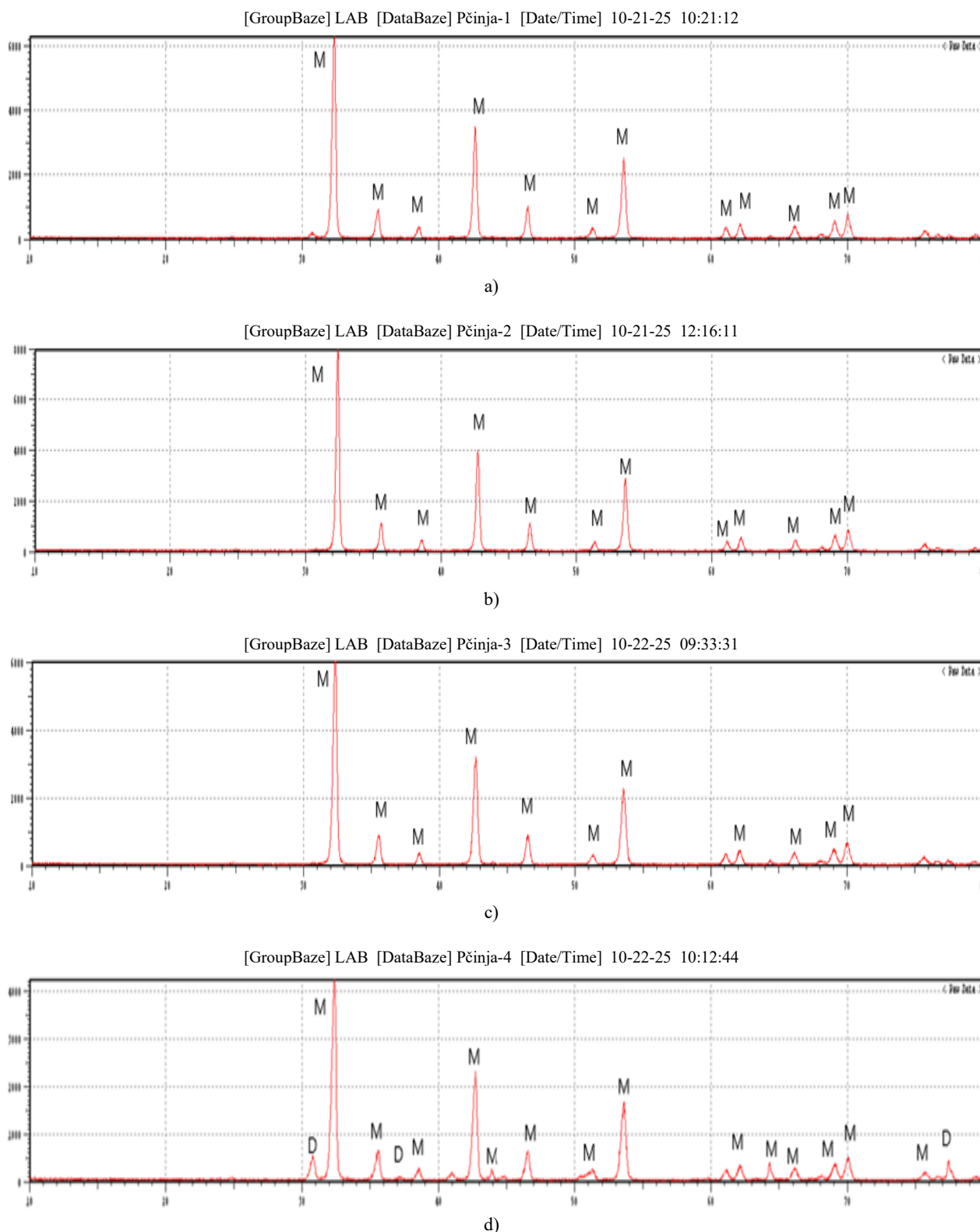


Fig. 13. XRPD patterns of the samples: a) sample 1; b) sample 2; c) sample 3; d) sample 4

Based on the XRD patterns recorded over  $2\theta = 10\text{--}70^\circ$  using Cu radiation, magnesite is the dominant crystalline phase. The strongest reflection at  $32.31^\circ$  together with the accompanying peaks at  $42.65^\circ$ ,  $46.50^\circ$ ,  $53.53^\circ$ ,  $62.08^\circ$ , and  $69\text{--}70^\circ$  match

magnesite well. The absence of a pronounced basal reflection near  $12^\circ$  indicates that serpentine is not dominant phase. The peak at  $30.75^\circ$  is dolomite,  $d = 2.905 \text{ \AA}$  is almost identical to the theoretical dolomite reflection at  $d = 2.886\text{--}2.904 \text{ \AA}$ . Additional

confirmation: the peaks at  $d = 2.525$  and  $d = 1.494$  are also dolomite, all three together form a classic dolomite set.

The unit cell parameters obtained using the main reflection lines of X-ray diffraction on sample

2 are:  $a = 4.63 \text{ \AA}$ ,  $c = 15.02 \text{ \AA}$ ,  $V = 279.35 \text{ \AA}^3$ . The obtained data are in accordance with the theoretical data by Deer et al. (1996); Bermanec (1999); Williams et al. (2003).

## CONCLUSION

Summarizing available data from this study, we conclude that the investigated sample is magnesite. Magnesite from the Pčinja river area most often occurs in the form of veins of varying thickness and length, with their orientation determined by the direction of faults and cracks. In certain parts of the terrain, the appearance of multiple subparallel veins is observed, while in other places they cross, branch or locally disappear and reappear. It appears as microcrystalline mass resembling unglazed porcelain. Its fracture is conchoidal, the hardness is  $3\frac{1}{2}$ – $4\frac{1}{2}$ , its streak is white and the density is  $3.0$ – $3.2 \text{ g/cm}^3$ .

Based on the XRD patterns recorded over  $2\theta = 10$ – $70^\circ$  using Cu radiation, magnesite is the dominant crystalline phase.

The unit cell parameters obtained using the main reflection lines of X-ray diffraction are:  $a = b = 4.71 \text{ \AA}$ ,  $c = 15.16 \text{ \AA}$ ,  $V = 291 \text{ \AA}^3$ .

The chemical data fully corroborates all previous SEM-EDX and XRD findings, confirming the Pčinja river area as a high-purity ophiolitic magnesite with characteristic ultramafic trace element signature (elevated Ni, Co) and minor dolomitic component. Co/Ni ratio  $\sim 0.1$  is typical of magnesite from ultramafic rocks. In addition to magnesite, the

presence of serpentine, dolomite and talc has also been determined.

Dolomite fits into the genesis as an indicator of the early phase of carbonization, and this is genetically very significant. During the initial carbonization of serpentinite,  $\text{CO}_2$ -rich fluids react with serpentine which also contains Ca (taken from pyroxenes). While Ca is still available in the system, Ca-Mg carbonate is formed dolomite. This occurs at relatively higher temperatures ( $\sim 350^\circ\text{C}$ ). When Ca is depleted from the system (excreted by fluids), reactions continue only with Mg pure, magnesite is formed. At the same time, Si released from the serpentine reacts with Mg and water to give talc. This occurs at lower temperatures ( $\sim 280^\circ\text{C}$ ). The dolomite in the examined samples (only 3 peaks, weak intensity) indicates that carbonization has proceeded quite far and most of the dolomite has already been converted to magnesite, and only a small relict amount remains. The serpentine is present but nearly consumed entirely. The Pčinja river area represents an advanced stage of carbonization where  $\text{CO}_2$ -rich hydrothermal fluids have converted  $\sim 85$ – $50$  90% of the original serpentinite to magnesite, with isolated serpentinite relic patches, only. This is entirely consistent with Type I cryptocrystalline magnesite deposits of the Balkan ophiolitic belt.

## REFERENCES

- Abdel-Aal, H. K. (2018): Production of magnesium chloride from seawater: Proposed method-preferential salt separation. In: *Magnesium: From resources to production*, pp. 53–64, CRC Press.  
<https://doi.org/10.1201/9781351170642>
- Abu-Jaber, N. S.; Kimberley, M. M. (1992): Origin of ultramafic-hosted vein magnesite deposits. *Ore Geol. Rev.*, 7, 155–191.
- Anthony, J. W., Bideaux, R. A., Bladh, K. W., Nichols, M. C. (Eds. (2003): *Handbook of Mineralogy*, Vol. 5: *Borates, Carbonates, Sulfates*. Mineral Data Publishing, Tucson, Arizona.
- Beinlich, A., John, T., Vrijmoed, J. C., Tominaga, M., Magna, T., Podladchikov, Y. Y. (2020): Instantaneous rock transformations in the deep crust driven by reactive fluid flow. *Nature Geoscience*, 13 (1), pp. 307–311.  
<https://doi.org/10.1038/s41561-020-0554-9>
- Bermanec, V. (1999): Systematic Mineralogy – Non-Silicate Minerals (in: Croatian), Targa, Zagreb, 264 p. ISBN 953-186-045-9.
- Boev, B. and Lepitkova, S. (2002): The age of ophiolite rocks in the territory of the Republic of Macedonia, *Proceedings of XVII Congress of Carpathian-Balkan Geological Association*, Bratislava, September 1, pp. 1335–0552.  
<https://eprints.ugd.edu.mk/id/eprint/1430>
- Božović, M., Prelević, D., Romer, R., Barth, M., Van Den Bogaard, P., Boev, B. (2013): Demir Kapija ophiolite: a snapshot of subduction initiation within a back-arc. *Journal of Petrology* 54, 1427–1453.

- Canterford, J. H. (2007): Magnesia – An important industrial mineral: A Review of Processing Options and Uses, Taylor Francis, pp. 57–104. Published online
- Coleman, R. G. (1977): Ophiolites: Ancient Oceanic Lithosphere? Berlin Springer-Verlag, 229 p. (Minerals and Rocks. Vol. 12, <https://doi.org/10.1007/978-3-642-66673-5>)
- Corre M., Brunet, R., Schwartz, S., Gautheron, C., Agraniar, A. Lesimple, S. (2023): Quaternary low-temperature serpentinization and carbonation in the New Caledonia ophiolite *Scientific Reports* **13** (1), Article number: 19413. DOI: 10.1038/s41598-023-46691-y
- De Obeso, J. C., Kelemen, P. B., Leong, J. M., Menzel, M. D., Manning, C. E. et al. (2022): Deep sourced fluids for peridotite carbonation in the shallow mantle wedge of a fossil subduction zone: Sr and C isotope profiles of OmanDP Hole BT1B. *Journal of Geophysical Research Solid Earth*, **127** (1), pp. 2169–9313. <https://doi.org/10.1029/2021jb022704>
- Deer, W. A., Howie, R. A., Zussman, J., and Chang, L. L. Y. (1996): Rock-forming Minerals, Volume 5B: Non-Silicates; Silicates, Sulphates, Carbonates, Phosphates and Hydrides, *Mineralogical Magazine*, **60** (400), pp. 539–540. DOI: 10.1180/minmag.1996.060.400.20
- Dilek, Y., and Furnes, H. (2011): Ophiolite genesis and global tectonics: Geochemical and tectonic fingerprinting of ancient oceanic lithosphere: *GSA Bulletin*, **123** (3–4), pp. 387–411. <https://doi.org/10.1130/B30446.1>
- Dilek, Y. and Furnes, H. (2014): Ophiolites and their origins. *Elements*, **10** (2), pp. 93–100, <https://doi.org/10.2113/gselements.10.2.93>
- Dimitrijević, M. D. (2001): Dinarides and the Vardar zone: a short review of the geology. *Acta Vulcanologica* **13** (1–2), pp. 1–8. <https://digital.casalini.it/10.1400/19061>
- Fallick, A. E., Ilich, M., Russell, M. J. (1991): A stable isotope study of the magnesite deposits associated with the Alpine-type ultramafic rocks of Yugoslavia. *Economic Geology* **86** (4): 847–861. <https://doi.org/10.2113/gsecongeo.86.4.847>
- Gartzos, E. (1986): *On the Genesis of Cryptocrystalline Magnesite Deposits in the Ultramafic Rocks of Northern Evia, Greece*. Doctoral Dissertation, ETH Zürich, Switzerland.
- Gartzos, E. (2004): Comparative stable isotopes study of the magnesite deposits of Greece. *Bulletin of the Geological Society of Greece*, **36** (1), pp. 196–203. <https://doi.org/10.12681/bgsg.16619>
- Hynes, A. (1975): Comment on “the troodos ophiolitic complex was probably formed in an island arc”, by A. Miyashiro. *Earth and Planetary Science Letters*, Vol. **25**, Issue 2, pp. 213–216, ISSN 0012-821X. [https://doi.org/10.1016/0012-821X\(75\)90198-3](https://doi.org/10.1016/0012-821X(75)90198-3)
- Jedrysek, M. O., Halas, S. (1990): The origin of magnesite deposits from the Polish Foresudetic Block ophiolites: Preliminary  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  investigations. *Terra Nova*, **2**, 154–159. <https://doi.org/10.1111/j.1365-3121.1990.tb00057.x>
- Jurković, I., Palinkaš, L. A., Garašić, V., Strmić Palinkaš, S. (2012): Genesis of vein-stockwork cryptocrystalline magnesite from the dinaride ophiolites. *Ophiolites*, **37** (1), 13–26. <https://doi.org/10.4454/ofioli.v37i1.403>
- Kahya, A., Kuşçu, M. (2016): Open system condition serpentinization of host-rock magnesite in Süleymaniye, Tutluca and Margı region of Eskişehir, NW Turkey. *Universal Journal of Geoscience* **4** (6), pp. 128–143. <https://doi.org/10.13189/ujg.2016.040603>
- Kelemen, P. B., Matter, J. (2008): In situ carbonation of peridotite for CO<sub>2</sub> storage. *Proceedings of the National Academy of Sciences of the United States of America* **105** (45): 17295–17300. <https://doi.org/10.1073/pnas.0805794105>
- Miyashiro, A. (1973): *Metamorphism and Metamorphic Belts*, Springer Nature. <https://doi.org/10.1007/978-94-011-6836-6>
- Moore, E. M., Vine, F. J. (1971): The Troodos Massif, Cyprus and other ophiolites as oceanic crust: evaluation and implications, *Philosophical Transactions of the Royal Society of London*. **268** (1192), pp. 443–466. DOI: 10.1098/rsta.1971.0006
- Peretti, A., Fumagalli, P., Ulmer, P., Günther, D. (1992): Petrology of wehrlites and dunites from the Totalp ultramafic massif (Davos, Switzerland), *Contributions to Mineralogy and Petrology*, **112**, 1–19.
- Pohl, W. (1989): *Comparative Geology of Magnesite Deposits and Occurrences*. Monograph Series on Mineral Deposits, No. 28, 1–13, Borntraeger, Berlin.
- Pohl, W. L. (1990): Genesis of magnesite deposits – Models and trends. *Geologische Rundschau*, **79**, pp. 291–299. <https://doi.org/10.1007/bf01830626>
- Pohl, W. L. (2011): *Economic Geology: Principles and Practice: Metals, Minerals, Coal and Hydrocarbons – Introduction to Formation and Sustainable Exploitation of Mineral Deposits*. Wiley-Blackwell. pp. 663.
- Prelević, D., Wehrheim, S., Božović, M., Romer, R., Boev, B. (2014): The origin of volcanic section of the Vardar ophiolitic zone: A comparative petrological and geochemical study of late-cretaceous volcanics from Macedonia with their Jurassic counterparts from Balkans, *XVI Serbian Geological Congress – Optimal Research and Sustainable Usage of the Geological Resources*.
- Reverdatto, V. V., Likhanov, I. I., Polyansky, O. P., Sheolev, V. S., Kolobov, V. Yu. (2018): *The Nature and Models of Metamorphism*, Chapter 4. Metamorphic processes in rocks. Springer Geology ISBN 978-3-030-03029-2 (eBook) <https://doi.org/10.1007/978-3-030-03029-2>
- Schroll, E. (2002): Genesis of Magnesites in the View of Isotope Geochemistry – IGCP 443 Magnesite and Talc. *Bole de Ciencias, Special Issue* **54**, Newsletter No. 2, Curitiba, Brazil, 59–68.
- Wang, Q. Q., Li, X. A., Wei, D. Z., Dai, S. J. (2011): The application of magnesite processing technics. *Applied Mechanics and Materials*, **71**, 2323–2326.
- Wicks, F. J., O'Hanley, D. S. (1988): Serpentine minerals: Structures and petrology. In: Bailey, S. W. (ed.), *Hydrous Phyllosilicates*. Reviews in Mineralogy, **19**, 91–167. Mineralogical Society of America.
- Williams, L. E., Szramek, J. K., Jin, L., Ku, C.W.T. and Walter, M. L., (2003). The carbonate system geochemistry of shallow groundwater-surface water systems in temperate glaciated watersheds (Michigan, USA): Significance of open-system dolomite weathering. *GSA Bulletin* 2007;; 119 (5-6): 515–528. doi: <https://doi.org/10.1130/B25967.1>
- Zedef, V., Russell, M., Fallick, A., Hall, A. (2000): Genesis of vein stockwork and sedimentary magnesite and hydromagnesite deposits in the ultramafic terranes of southwestern Turkey: A stable isotope study. *Economic Geology* **95** (2), 429–445. <https://doi.org/10.2113/gsecongeo.95.2.429>

## Резиме

МИНЕРАЛОГИЈА НА МАГНЕЗИТОТ ОД ОБЛАСТА НА РЕКАТА ПЧИЊА,  
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**Клучни зборови:** магнезит; серпентин; талк; ултрабазични карпи; река Пчиња

Во овој труд е претставена минералозна карактеризација на магнезитот од областа на реката Пчиња. Идентификацијата на испитуваните минерални примероци беше извршена со оптички микроскоп, скенирачки електронски микроскоп (SEM/EDS), скенирачка електронска микроскопија, индуктивно спрегната плазма/масена спектроскопија (ICP/MS), и рендгенска дифракција на прав (XRPD). Врз основа на сите добиени резултати може да се заклучи дека испитуваните примероци се магнезит. Магнезитот од областа на реката Пчиња најчесто се јавува во форма на жили со различна дебелина и должина, а нивната ориентација е одредена од насоката на раседите и пукнатините. Во одредени делови од теренот се забележува појава на суб-паралелни жили, додека на други места тие се вкрстуваат, се разгрануваат или локално исчезнуваат и повторно се појавуваат. Магнезитот се јавува како микростална маса слична на неглазиран порцелан. Прекршувањето е неправилно до школкасто. Тврдоста е  $3\frac{1}{2}$ – $4\frac{1}{2}$ , а густината од 3,0 до 3,2 g/cm<sup>3</sup>. По боја е бел. Според резултатите од рендгенскиот дијаграм магнезитот е доминантна кристална фаза. Параметрите на елементарната ќелија се:  $a = b = 4,71 \text{ \AA}$ ,  $c = 15,16 \text{ \AA}$ ,  $V = 291 \text{ \AA}^3$ . Резултатите од хемиските анализи целосно ги потврдуваат податоците од SEM и XRD.

Односот Co/Ni  $\sim 0,1$  е типичен за магнезит од ултрамафични карпи. Доломитот се вклопува во генезата како индикатор за раната фаза на карбонизација, а ова е генетски многу значајно. За време на почетната карбонизација на серпентинот, течностите богати со CO<sub>2</sub> реагираат со серпентин, кој исто така содржи Ca (земен од пироксените). Додека Ca е сè уште достапен во системот, се формира Ca-Mg карбонатен доломит. Ова се случува на релативно високи температури ( $\sim 350 \text{ }^\circ\text{C}$ ). Кога калциумот е исцрпен од системот, реакциите продолжуваат само со магнезиум и вода и се формира талк. Ова се случува на пониски температури ( $\sim 280 \text{ }^\circ\text{C}$ ). Доломитот во испитуваните примероци укажува дека карбонизацијата напреднала и поголем дел од доломитот веќе е претворен во магнезит, а останува само мала реликтна количина. Серпентинот е присутен многу малку. Областа на Пчиња претставува напредна фаза на карбонизацијата каде што хидротермалните течности богати со CO<sub>2</sub> претвориле  $\sim 85$ – $90\%$  од оригиналниот серпентин во магнезит, при што се останати само изолирани реликтни делови од серпентин. Ова е целосно во согласност со кристокристалните магнезитни наоѓалишта од тип I од балканскиот офиолитски појас.

