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GEOME 2
Manuscript received: December 20, 2018
Accepted: Mayr 15, 2019

Geologica Macedonica, Vol. **33**, No. 1, pp. 53–59 (2019)
IISSN 0352 – 1206
e-ISSN 1857 – 8586
UDC: 549.623.086:553.548(497.785)

Original scientific paper

PRELIMINARY INVESTIGATIONS OF PARAGONITE IN MARBLES FROM SIVEC, NORTH MACEDONIA

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Abstract: This paper presents preliminary results of investigation of the paragonite crystals in marbles from Sivec. Investigated samples were analyzed by IR, SEM and XRD methods. Paragonite from Sivec has light apple-green colour. It occurs in small nodules found generally in fine-grained parts and in cleavages of the white dolomitic marble. Paragonite crystals are greasy to the touch. The luster of its small scales resembles that of the sericite. Crystals are thin and tabular II {001}, commonly fine scaly. Crystal system is monoclinic, 2/m. Cleavage is perfect II {001}. The presence of paragonite indicates that the muscovite is saturated with the sodium component and that the assemblage lies on a section of the multi component solvus between the muscovite and paragonite end members. In this case we have transition from muscovite to paragonite. The concentration of Na increases (0.87–4.52), while the concentration of K is decreasing (4.62–0.32). The most intense registered maxima in the studied X-ray powder diagram were compared with the corresponding maxima in the diagram of paragonite 1M, ICDD 00 0420602. The unit cell parameters obtained using the main reflection lines of X-ray diffraction are: $a = 5.124$ Å; $b = 8.890$ Å; $c = 19.324$ Å; $\beta = 94.06°$; $V = 878.1$ Å^3.

Key words: paragonite; muscovite; marble; Sivec

INTRODUCTION

The Sivec deposit is situated some 10 km northeast of Prilep at the crosscut between the Babuna and Kozjak mountains. The marbles of the marble mass Sivec are part of the Precambrian Pelagonian marble series, which is preserved along the east peripheral part of the Pelagonian crystal mass. The geological setting of the immediate surroundings of the deposit includes the following members: Neogene and Quaternary sediments; Riphean-Cambrian metamorphic complex (filithioids, metadiabazes, amphibole shales and marbles); granitoides; marble series [a) dolomite and calcite-dolomite marbles, b) calcite marbles]; mixed series (albitic gneiss, micaschists, marbles and cypolines); gneiss-micaschists series (gneisses, micaschists, quartzites and amphibolites) (Figure 1).

The major lithostratigraphic features of the Pelagon result from the primary accumulation of pelitic-psammitic and carbonate sediments accompanied by poorly expressed initial magmatism. Over the Grenville orogenesis, the complexes have been affected by metamorphic-magmatic and tectonic processes when they metamorphosed into metamorphic rocks of epidote-amphibolite faces.

The marble mass extends to the northwest–southeast 4 km long and 2 km wide, with an inclination towards the northeast at an angle of 25°– 40°.

Generally, the lowermost portions of the marble mass in Sivec consist of white dolomite marbles of granoblastic composition and massive texture. According to the mineralogy, structural and textural composition, the marble mass in Sivec is built of saharoid white dolomitic marble, dolomitic marble with jets, nests and tracks of calcite and fine-grained calcite marbles.

Saharoid white dolomite marbles have been developed at the lowest levels. By colours are white, fine grains, homogeneous, massive and compact. Their dolomitic composition is partly related to primary gneiss. Structural researches of the Sivec marbles are made by Dumurdžanov and Stefkov (1994).

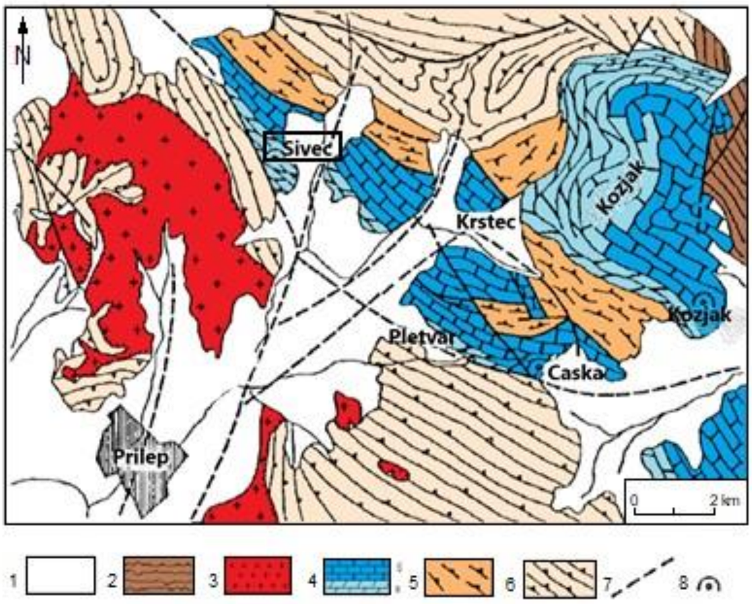

Fig. 1. Geological map of the area with marble mass Sivec-Pletvar-Kozjak (Dumurdžanov et al., 1990), R = 1:18000
Legend: 1. Neogene and Quaternary sediments; 2. Riphean-Cambrian metamorphic complex (filithioids, metadiabazes, amphibole shales and marbles); 3. granitoides; 4. marble series [a) dolomite and calcite-dolomite marbles, b) calcite marbles]; 5. mixed series (albitic gneiss, micaschists, marbles and cypolines); 6. gneiss-micaschists series (gneisses, micaschists, quartzites and amphibolites); 7. fault; 8. surface excavation of marbles

Whiteness, homogeneity and compactness are associated with the thermal effect and metamorphic processes of Pelagonia granitoids. The influence of granitoids on marbles is also seen in the appearance of minerals such as corundum, fluorite, paragonite, titanite, epidote, and others which are not observed to others places.

Paragonite [$NaAl_2(AlSi_3O_{10})(OH)_2$] has been conventionally considered as metamorphic mineral, the first appearance of which indicates – with other minerals – the beginning of metamorphism (Winkler, 1979).

The name of the paragonite came from the Greek λανθασμένη αντίληψη, for misleading, as it looks like talc.

Paragonite from Sivec has light apple-green colour (Figures 2–3). It occurs in small nodules and impregnations found generally in fine-grained parts and in cleavages of the white dolomitic marble. Paragonite occurences are greasy to the touch. The luster of its small scales resembles that of the sericite. Crystals are thin tabular II {001}; commonly fine scaly. Crystal system is monoclinic, 2/m. Cleavage is perfect {001}.

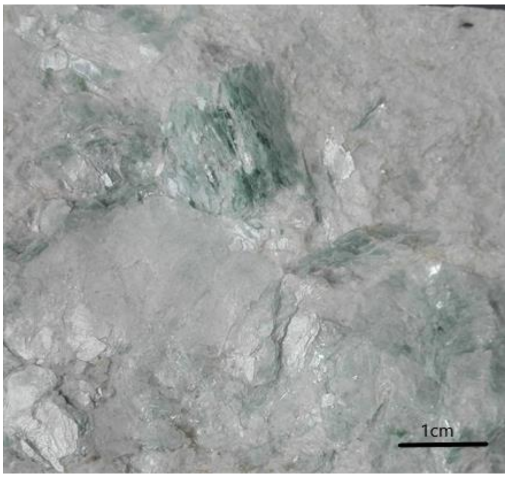

Fig. 2. Light apple-green paragonite in marbles from Sivec

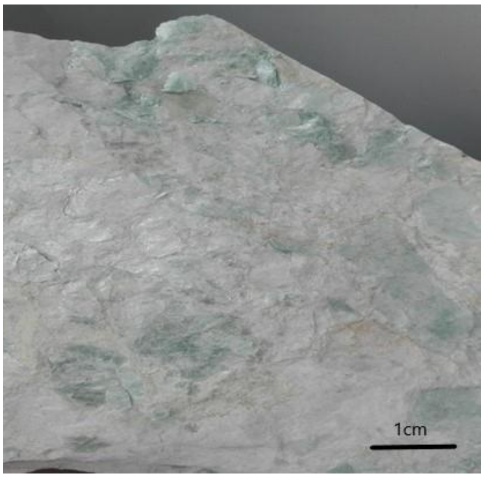

Fig. 3. Light apple-green paragonite in marbles from Sivec

The micas, which are common rock-forming minerals, include white micas muscovite, margarite, and paragonite, and the dark micas which may be broadly described as the biotites. These micas are extremely useful as petrogenetic indicator phases.

The compositional join between the muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$] and paragonite [$NaAl_2$ (Al $Si_3O_{10})(OH)_2$] end-members is represented by the Na and K substitution.

A preliminary phase diagram was prepared by Yoder and Eugster (1954) for the pseudobinary system muscovite-paragonite. They concluded that each mica is appreciably soluble in the other, that the maximum solubility occurs at about 660°C, and that the degree of solubility is markedly temperature dependent. The maximum solubility of paragonite in muscovite is given as 24% and that of muscovite in paragonite as 20%, both at 2 kilobars pressure and 650 °C using glasses of the required composition as starting materials. Their data suggest that the system might be used as a geologic thermometer, by determining the spacing of one mica when both are present.

At high temperatures the muscovite–paragonite solvus tends to close, whereas at low temperatures the solvus opens and potassium–sodium rich white mica may coexist (Guidotti, 1976, 1984). The temperature dependence of the K–Na partitioning works well as a qualitative geothermometer, whereas its use as a quantitative geothermometer is not very successful (Guidotti, 1984). Detailed examinations for paragonite-muscovite solvus, the effect of ferromagnesian components on the paragonite-muscovite solvus and the contrasting response of muscovite and paragonite to increasing pressure are given by Guidotti et al. (1994a, 1994b, 2000).

According to Frey (1969, 1978, 1987) and Livi et al. (1988, 1990) the degree of solid solution in coexisting muscovite and paragonite has been shown to increase with increasing grade and therefore, with temperature in natural samples.

ANALYTICAL METHODS

For reliable characterization of the mineral species in our research following analytical methods were used: Fourier transform infrared spectroscopy using diffuse reflectance method (FTIR/DRS), scanning electron microscopy (SEM), coupled with energy dispersive X-ray spectrometer (EDS), and X-ray powder difraction (XRPD).

Infrared spectroscopy. The analyses were accomplished by using an IRPrestige 21 spectrophotometer (Shimadzu, Japan). The spectra were recorded in spectral range 400–4000 cm^{-1} at a resolution of 2 cm^{-1} and 45 scans. For the spectra manipulation was used IRSolution 1.5 software (Shimadzu Corporation). Two methods were employed in these measurements:

a) The KBr pellet method. The pellets (4 mm dia) were prepared by mixing 0.5–1 mg of the sample powder and about 100 mg of the KBr.

b) The diffuse reflectance spectroscopy (DRS). The measurements were performed by use of DRS 8000 (Shimadzu, Japan) attachment. The powdered sample was diluted to about 5% by weight in KBr and placed into the sample holders (2 mm dia with 1 mm deep). The infra red spectra were obtained by measuring the diffuse reflected light that was emerged from the sample surface after the first being absorbed inside the sample and reflected among the particles. The resultant spectra were converted to Kubelca-Munk function (Griffiths, 2007) to make them more comparable to the absorption spectra.

Scanning electron microscopy **(**SEM) is model VEGA3LMU, increasing 2×1000 000, W-wire, voltage up 200 V to 20 kV, infrared camera, maximum sample size 81 mm height, 30 mm width. The standards used are as follows: O: SiO_2; Na: albite; Mg: MgO; Al: Al_2O_3; Si: SiO_2; P: GaP; Ca: wollastonite; Ti: Ti; Fe: Fe; Br: KBr. Results of SEM/EDS analyses of mineral phases demonstrated usefulness of this method for identification and characterization of mineral phases whose size is often below the resolution of an optical microscope.

XRD. Powder X-ray analysis was performed on a diffractometer (Shimadzu) XRD-6100, 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 is finely ground, homogenized, and average bulk composition is determined. The most intense registered maxima in the studied powder diagrams were compared with the corresponding diagrams from PDF-2 software. Unit Cell software (Tim Holland & Simon Redfern, update 16th Feb 2006) was used for calculation on unit cell data.

RESULTS AND DISCUSSION

The mineral specimen from Sivec was first analyzed by use of FTIR-DRS spectroscopy. The IR measurements were performed on several samples, including not dried and samples dried at 105° C for 1 h. All samples exhibit similar spectral profile, demonstrating the presence of calcite and silicate phase, as it is shown in Figure 4. The presence of calcite was identified by the IR bands at 2983, 2875, 2514, 2142, 1795, 1442, 876 and 712 cm^{-1} (Jovanovski et al., 2002, Chukanov, 2013), as well as by comparing the spectra with a referent spectrum of calcite, Kemika – Zagreb (Figure 4).

In the hydroxyl stretching region, all samples depicted well resolved IR band with a maximum centred at 3635 cm^{-1} attributed to the structural OH^{-} groups. The very weak band observed in the 3200–3400 cm^{-1} region in line with the band at 1645 cm^{-1}, prescribed to H_2O stretching and bending vibrations, respectively, suggests small amount of adsorbed water. The broad and complex band observed in the 950–1150 cm^{-1} spectral region corresponds to the Si-O-Si or Si-O-Al stretching modes. In addition, the weak bands registered at 810 and 750 cm^{-1} (overlapped with band of CO_3 vibrations) are attributable to Al-O and Al-O-Al stretching modes. In the lower wave number region, the band at around 530 cm^{-1} was found to be the most prominent, in all recorded spectra. According to the IR data reported in the literature, this band coincides with bending Si–O–Si modes in some phyllosilicates such as muscovite and paragonite (Shimoda and Brydon, 1971; Farmer, 1974; Langer et al., 1981; Kloprogge et al., 1999; Beran, 2002, Šontevska et al., 2008; Chukanov, 2013; Jovanovski and Makrevski, 2016).

The results of chemical analyses for investigated samples obtained by SEM-EDS are given in Figures 7 and 8 and Table 1, while BSE images of analyzed areas are given in Figures 5 and 6.

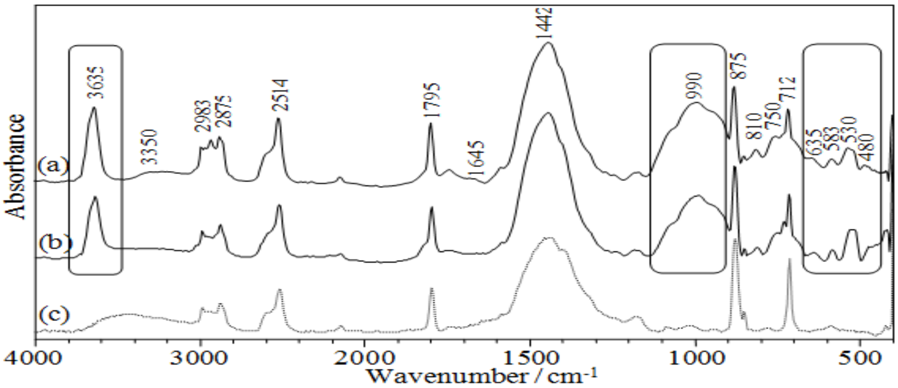

Fig. 4. IR spectra: (a) a sample before drying, (b) after drying and (c) referent spectrum of calcite. Marked regions designate the presence of silicate phase.

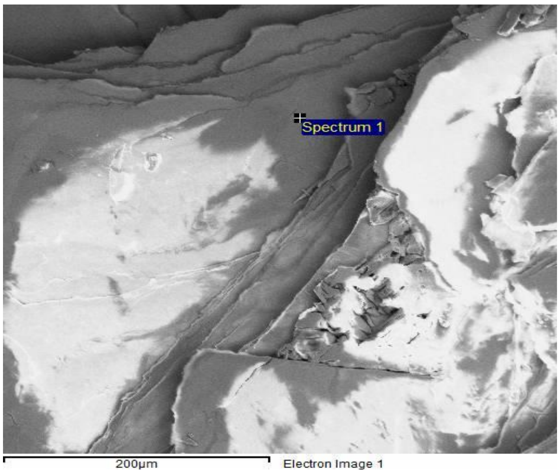

Fig. 5. SEM image of muscovite (spectrum 1), sample 1

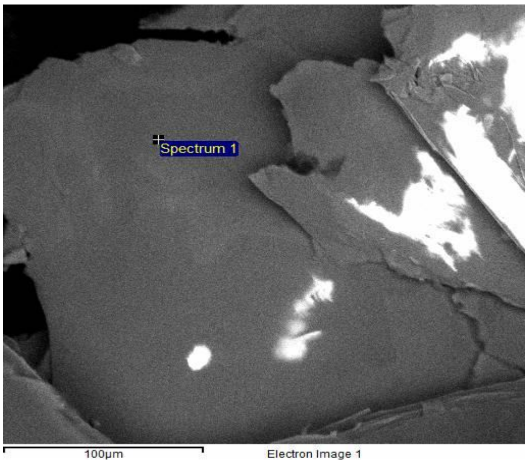

Fig. 6. SEM image of paragonite (spectrum1), sample 2

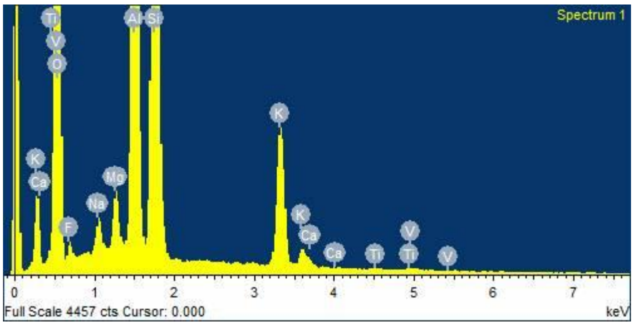

Fig. 7. EDX spectrum 1 of muscovite, sample 1

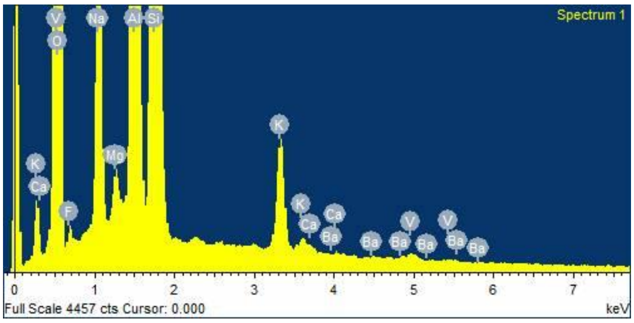

Fig. 8. EDX spectrum 1 of paragonite, sample 2

Table 1

Chemical composition of muscovite and paragonite from Sivec by SEM-EDX

Element	Weight %	Weight %
	Spectrum 1 sample 1	Spectrum 1 sample 2
O	62.08	57.61
F	3.01	0.92
Na	**0.87**	**4.52**
Mg	1.05	0.34
Al	13.02	16.52
Si	16.11	18.49
K	**4.62**	**0.32**
Ca	0.12	0.08
Ti	0.06	–
V	0.06	0.11
Ba	–	0.07
Totals	100.00	100.00

From the data on chemistry given in Table 1 can be concluded that the examined sample 1 is muscovite, while sample 2 is paragonite. Basic formula on muscovite is $K_2Al_4\,[Si_6Al_2O_{20}](OH,F)_4$. Na may replace K in muscovite to form a paragonite with similar optical properties. Several reviews of the occurrences and crystal chemistry of micas have been written (Guidotti, 1984).

The presence of paragonite indicates that the muscovite is saturated with the sodium component and that the assemblage lies on a section of the multicomponent solvus between the muscovite and paragonite end members.

In this case we have transition from muscovite to paragonite. The concentration of Na increases (0.87–4.52), while the concentration of K is decreasing (4.62–0.32).

In Figure 9 is given an XRD pattern of the investigated paragonite.

The most intense registered maxima in the studied X-ray powder diagram were compared with the corresponding maxima in the diagram of paragonite 1 M, ICDD 00 0420602.

The unit cell parameters obtained using the main reflection lines of X-ray diffraction are: a = 5.124 Å; b = 8.890 Å; c = 19.324 Å; β = 94.06°; V = 878.1 Å^3.

Comparison of unit cell data on the examined paragonite with data reported by RRUFF (Zen, Ross Bearth, 1964) and Weinrich minerals (Lin and Bailey, 1984) is given in Table 2.

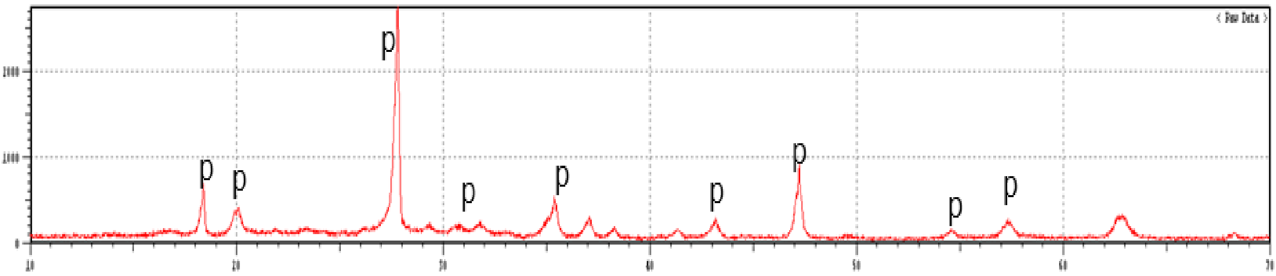

Fig. 9. XRD pattern of the investigated paragonite

Table 2

Comparison of unit cell data on the examined paragonite with data reported by Zen, Ross and Bearth (1964) and Lin and Bailey (1984)

	Paragonite from Sivec	Literature data RRUFF, ID:R050447.1 (Zen E-A., Ross M., Bearth P., 1964)	Literature data Weinrich minerals (Lin and Bailey,1984)
Crystal system, space group	Monoclinic, C2/m	Monoclinic C2/m	Monoclinic C2/m
Unit cell dimension	a = 5.124 Å b = 8.890 Å c = 19.324 Å β = 94.06°	a = 5.119 Å b = 8.881 Å c = 19.326 Å β = 94.57°	a = 5.13 Å b = 8.89 Å c = 19.32 Å β = 95°
Volume	878.1 Å^3	877.8 Å^3	877.75 Å^3

CONCLUSION

Summarizing available data from this study we concluded that investigation sample is paragonite. Paragonite from Sivec has light apple-green colour. It occurs in small nodules and impregnations found generally in fine-grained parts and in cleavages of the white dolomitic marble. Paragonite inclusions are greasy to the touch. The luster of its small scales resembles that of the sericite. Crystals are thin tabular II {001}; commonly fine scaly. Crystal system is monoclinic, 2/m. Cleavage is perfect {001}. The presence of paragonite indicates that the muscovite is saturated with the sodium component and that the assemblage lies on a section of the multicomponent solvus between the muscovite and paragonite end members. In this case we have transition from muscovite to paragonite. The concentration of Na increases (0.87–4.52), while the concentration of K is decreasing (4.62–0.32). The most intense registered maxima in the studied powder diagram were compared with the corresponding maxima in the diagram of paragonite 1 M, ICDD 00 042 0602.

The unit cell parameters obtained using the main reflection lines of X-ray diffraction are: a = 5.124 Å; b = 8.890 Å; c = 19.324 Å; β = 94.06°; V = 878.1 Å^3.

We hope that the results of this research will become the basis for further detailed research on the muscovite-paragonite transition.

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Резиме

ПРЕЛИМИНАРНИ ИСТРАЖУВАЊА НА ПАРАГОНИТОТ ВО МЕРМЕРИТЕ ОД СИВЕЦ, СЕВЕРНА МАКЕДОНИЈА

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Клучни зборови: мермер; парагонит; мусковит; рендгенска дифракција

Во овој труд се презентираат резултати од прелиминарните истражувања на кристалите на парагонит кои се појавуват во мермерите од Сивец.

Испитаните примероци беа анализирани со IR, SEM и XRD методи. Парагонитот од Сивец има светлозелена боја. Се појавува во мали нодули и импрегнации, најчесто пронајдени во ситнозрнести делови и во пукнатини на белиот доломитски мермер. Сјајноста е масна, слична на сјајноста на серицит. Се јавува во тенки ливчиња паралелни со {001}. Кристализира во моноклиничен систем, 2/m. Цепливоста е совршена по {001}. Присуството на парагонит во мермерот од Сивец е резултат на заситувањето на мусковитот со натриум кој го заменува калиумот, при што мусковитот преминува во парагонит. Концентрацијата на Na се зголемува (0,87–4,52), додека концентрацијата на K се намалува (4,62–0,32).

Добиените податоци од рендгенските дифракциони испитувања се споредени со соодветните максимуми од дијаграмот на парагонит 1M, ICDD 00 0420602.

Со добиените податоци од рендгенските дифракциони испитувања се пресметани димензиите на елементарната ќелија. Добиени се следниве резултати: a = 5.124 Å; b = 8,890 Å; c = 19,324 Å; β = 94,06°; V = 878.1 Å^3.

Се надеваме дека резултатите од ова истражување ќе послужат како основа за понатамошни детални истражувања кои ќе се однесуват пред сè на преминот на мусковитот во парагонит.