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PRELIMINARY INVESTIGATIONS OF GOETHITE AND MONAZITE FROM SIVEC, REPUBLIC OF NORTH MACEDONIA

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A b s t r a c t: This paper presents the preliminary investigations of goethite and monazite that appear in marbles from Sivec. The presence of these minerals was not previously reported in the Sivec marbles that, along with the dominant dolomite and calcite, also revealed the presence of a vast number of other minerals including fluorite, rutile, phlogopite, corundum, diaspore, almandine, clinochlore, muscovite, quartz and zoisite. Goethite [$Fe^{3+}O(OH)$] from Sivec occurs in small crystals found generally in fine-grained parts of the white dolomitic marble. The color ranges from yellow-brown to nearly black, and the luster varies correspondingly from earthly to submetallic. Cleavage is perfect {010} and less perfect {100}. The streak is yellowish brown. The size of the goethite crystals is 1 cm. The crystal system is orthorhombic. *Point Group:* 2/m 2/m 2/m, *Space Group*: Pbnm. The *unit cell* parameters obtained using the strongest X-ray diffraction peaks are: a = 4 .617 Å, b = 9.976 Å, c = 3.024 Å, Z = 4, V = 139.32 Å^3. Monazite crystals are found on the surface of the goethite crystal. The size of the crystals within size varies in length (21.88 – 53.61 μm) and width (8.45 – 20.38 μm).

Key words: Sivec; marble; goethite; monazite

INTRODUCTION

The marbles mass from Sivec is a part of the Precambrian Pelagonia marble series, which is preserved along the eastern peripheral part of the Pelagonia crystalline mass. The geological setting of the immediate vicinity of Sivec includes the following members: Neogene and Quaternary sediments; the Riphean Cambrian metamorphic complex (phyllithioids, metadiabases, amphibole schists and marbles); granitoids; marble series: a) dolomites and calcithecal marbles, b) calcite marbles; mixed series (albite gneisses, micaschists, marbles and cipolins); series of gneissic micaschists (gneisses, micaschists, quartzites and amphibolites) (Figure 1). The main lithostratigraphic features of Pelagonia derive from the primary accumulation of pelitic-psamitic and carbonate sediments accompanied by poorly expressed initial magmatism. In general, the lowest parts of the marble mass in Sivec consist of white dolomitic marbles of a granolastic composition and massive texture. According to the mineralogy, structural and textural composition, the marble mass in Sivec is made of sucrose white dolomitic marble, dolomitic marble with planes, nests and calcite, and finely crafted calcite marble. Their dolomite composition is partly related to the primary gneiss. The structural features of the marbles from Sivec are reported by Dumurdžanov and Stefkov (1994).

The Sivec marble mass has exceptional, unique petrographic and mineralogical characteristics in terms of their structure and present mineral association that is a consequence of the specific genesis of this part of the Pelagonia marble metamorphic complex. Dolomite grain size ranges from 0.1 to 0.5 mm. The grains are partially rounded and exhibit pronounced crushing. Dolomite grains rarely have an irregular polygonal shape.

The influence of the granites that are near the marble mass is manifested by a higher presence of corundum, fluorite, paragonite, fangite, titanite, rutile, epidotic minerals, chlorite, diaspore and others.

The mineralogy of marbles from Sivec was previously investigated by several research groups: Erdmannsdorfer (1925), Barić (1960, 1969), Stojanov (1960, 1967, 1968), Jeršek and Mitrič (1999), (Jovanovski et al. (2012), Boev (2015), Šijakova-Ivanova and Petreski (2018), Šijakova-Ivanova and Robeva Čukovska (2019). In all of the mentioned papers, the presence of goethite and monazite was not reported.

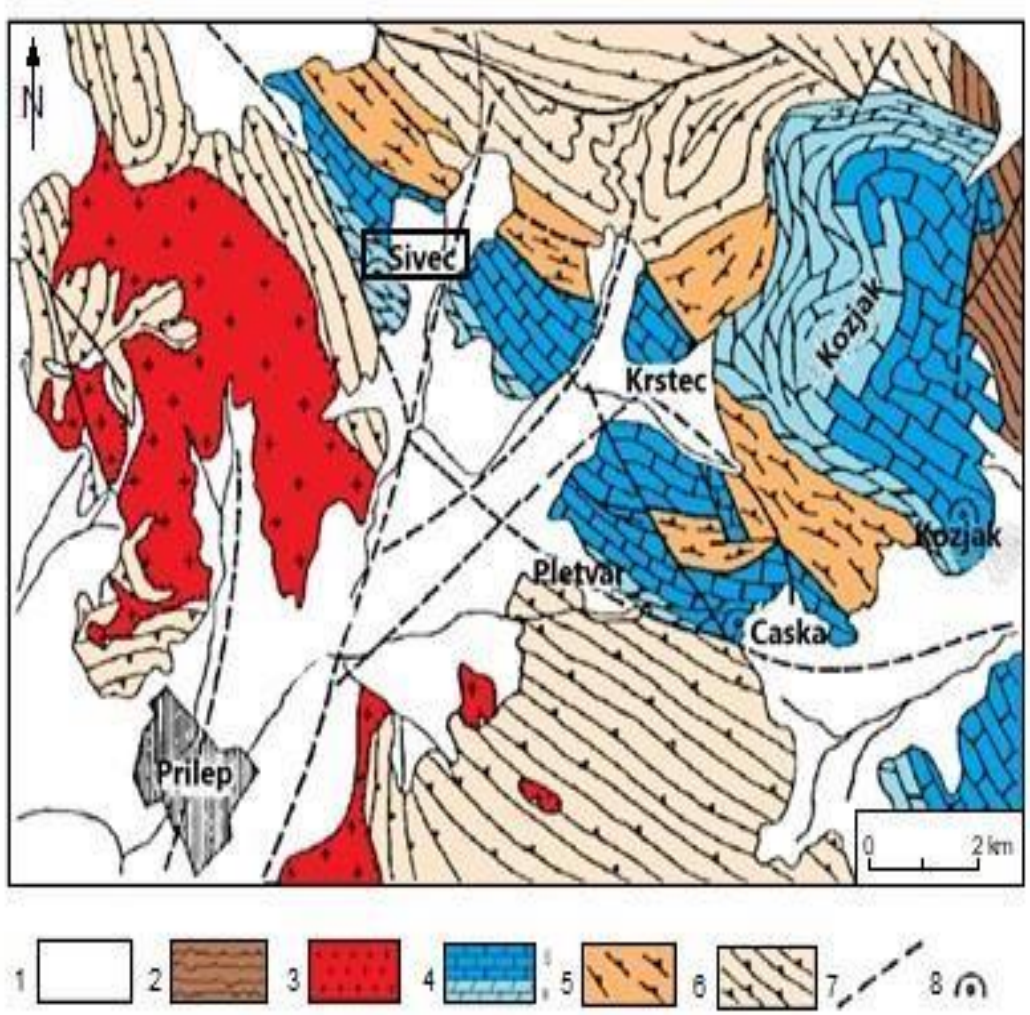


Fig. 1. Geological map of the area with the marble mass of Sivec-Pletvar-Kozjak (Dumurdžanov et al., 1990), R=1:18000. Legend: 1. Neogene and Quaternary sediments; 2. Riphean-Cambrian metamorphic complex (filithoids, metadiabazes, amphibole shales and marbles); 3. granitoides; 4. marble series; 5. mixed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

ANALYTICAL METHODS

For our research, the following analytical methods were used: Fourier transform (FT) infrared spectroscopy, scanning electron microscopy coupled with energy dispersive X-ray spectrometer, and X-ray powder diffraction.

Infrared spectroscopy. The FT infrared spectrum of the goethite sample was recorded on the IR-Prestige 21 spectrometer (Shimadzu, Japan) using the KBr pellet method, in the spectral range of 400–4000 cm^{-1} at a resolution of 2 cm^{-1} and 60 scans. The pellet was prepared by mixing 0.3 mg of the sample powder and 100 mg of KBr. The spectra manipulation was performed by using the IR Solution 1.5 software (Shimadzu Corporation).

Scanning electron microscopy SEM analyses and electron micro-photographs were conducted using a VEGA3- LMU scanning electron microscopy. The study utilized semi-quantitative analysis using appropriate standards. 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. The results of the SEM/EDS analyses of mineral phases demonstrated the adequacy of this method for identification and characterization of mineral phases whose size is often below the resolution of an optical microscope.

XRD analyses were carried out by conventional X-ray diffraction techniques using the (Shimadzu) XRD-6100 diffractometer with CuKα (1.54178) radiation operating at 40 kV and 30 mA. The powdered sample was scanned over the 10–80° range with a step size of 0.02° and scanning speed of 1.2°/min. The most intense registered maxima in the studied powder diagrams were compared with the corresponding diagrams from the ICDD PDF-2 software (2019). The Unit Cell software (Holland & Redfern, update 16th April 2006) was used for calculation on unit cell data.

RESULTS AND DISCUSSION

The goethite [$Fe^{3+}O(OH)$] from Sivec occurs in small crystals found generally in fine-grained parts of the white dolomitic marble. The color ranges from light brown to nearly black and the luster varies from earthly to submetallic (Figure 2). The cleavage is perfect {010} and less perfect {100}. The streak is yellowish brown. The size of the goethite crystals is 1 cm.

Fig. 2. Crystal of goethite (1 cm length and 1cm width)

Showing the IR spectra characterization of limonite minerals, Makreski et al. (2004) revealed the occurrence of goethite (α-FeOOH) in the Allchar site and lepidocrocite (γ-FeOOH) from Pehčevo.

The IR spectrum of the examined sample of goethite is shown in Figure 3. The obtained data together with the corresponding literature data are shown in Table 1.

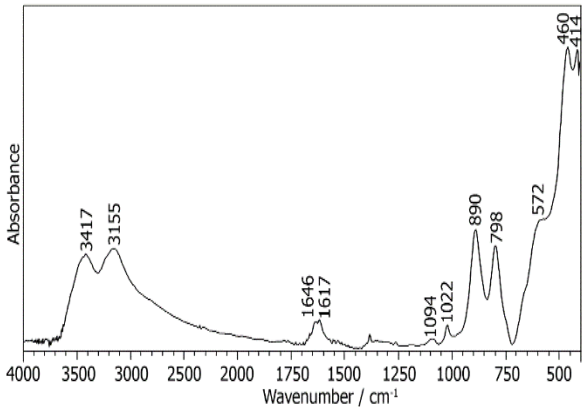


Fig. 3. Infrared spectrum of the goethite sample

T a b l e 1

IR data of the examined sample from Sivec, compared with literature data

This work	Makreski et. al., 2004	Chukanov, 2014	Ruan et. al., 2002	
Goethite (Sivec)	Goethite (Allchar)	Goethite (Attica, Greece)	Goethite (Unheated)	
3417	3419	3300sh	3479	ν(H-O-H)
3155	3117	3120s	3206	ν(OH)
1646	1637	1655w	1686	δ(O-H)
1617			1637	γ(O-H)
1094	1096	–	–	–
1022	1017	1030sh	–	–
890	893	894	890	δ(OH)
798	799	797	799	γ(OH)
–	667	655sh	–	–
572	570	595	–	–
460*	472	465s	–	–
417*	407	412s	–	–

* Ascribed to ν(Fe-O…Fe) by Plyusnina (1977), cited by Makreski et. al., 2004

The most obvious spectral feature is the appearance of two well-separated bands at 890 and 798 cm^{-1} attributed to the hydroxyl deformation modes in the goethite structure. In the hydroxyl stretching region, two prominent bands at 3417 and 3155 cm^{-1} are observed. The band at 3155 cm^{-1} is located in a sub-region attributable to the stretching vibration of O-H units in goethite (Ruan et al., 2002). The band at 3417 cm^{-1} in line with the bands at 1646 and 1617 cm^{-1} can be assigned to the ν(H–O–H) and δ(H–O–H), respectively. These bands are indicative for the presence of non-stoichiometric hydroxyl units in the goethite structure (Ruan et al., 2002). Furthermore, the IR spectrum shows two less intensive distinct bands at 1096 and 1022 cm^{-1} which could be related to the characteristic modes of other minerals. Thus, it can be assumed that a small amount of additional mineral phase is also present in the goethite sample. The lower wavenumber region exhibits an intense band with two separated maxima (460 and 417 cm^{-1}) and shoulder at 570 cm^{-1} which, according to Plyusnina (1977) and (Makreski et. al. (2004), are associated with ν(Fe-O).

The results of the chemical analyses for the examined goethite and the comparison with literature data (Deer et al., 1962) are given in Figure 4 and Table 2.

The presence of Cu in the examined sample was determined, which can be seen from Table 2. The incorporation of Cu in the structure of natural goethite is more surprising because this element has a lower geochemical affinity for Fe oxides and a higher affinity for Mn oxides and phyllosilicates (Manceau et al., 2000). Other elements, which are commonly associated in goethite, such as Al, Si, P and Mn, were not detected in the goethite sample from Sivec.

On the surface of the goethite crystal, small monazite crystals were identified. Monazite is a rare earth phosphate mineral REE(PO_4) containing mostly light REE and some heavy REE, more than bastnäsite (Kanazawa and Kamitani, 2006).

The generic chemical formula for monazite, (Ce, La, Nd, Th) (PO_4, SiO_4), reveals that cerium, lanthanum, neodymium and thorium can substitute for one another in the mineral's structure, and substitution of silica for phosphate also occurs.

According to George Blankson (Abaka-Wood et al., 2019), the REE minerals (bastnäsite, monazite, florencite, stillwellite, brannerite and stetindite) identified were in intimate associations with weakly ferromagnetic/strongly paramagnetic iron oxides (mainly hematite and goethite) and diamagnetic silicate (quartz, illite and annite) minerals.

The results of chemical analyses for monazite and comparison with literature data (Palache et al., 1951) are given in Figure 5 and Table 3.

The size of the monazite crystals varies in length 21.88 – 53.61 μm and width 8.45 – 20.38 μm.

Figure 6 represents the XRPD pattern of the investigated goethite.

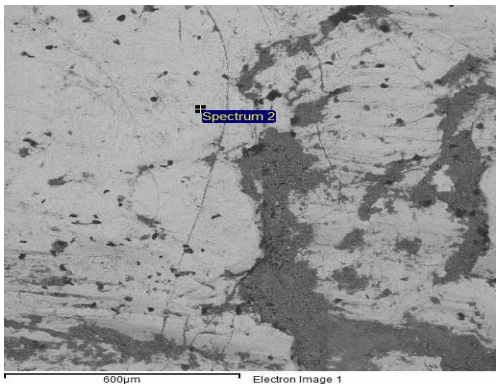
The most intense registered maxima in the studied X-ray powder diagram were compared with the corresponding maxima in the diagram of goethite, ICDD 00 017 0536. The strongest peak is obtained at 2θ around 21°. This result is in compliance with that of Villacís-García et al. (2015), which reported goethite exhibits the highest peak intensity at 2θ (21°).

The unit cell parameters obtained using the main reflection lines of X-ray diffraction are a = 4.617 Å, b = 9.976 Å, c = 3.024 Å, Z = 4, V = 139.32 $Å^3$. The crystal system is orthorhombic. *Point Group:* 2/m 2/m 2/m, *Space Group*: Pbnm.

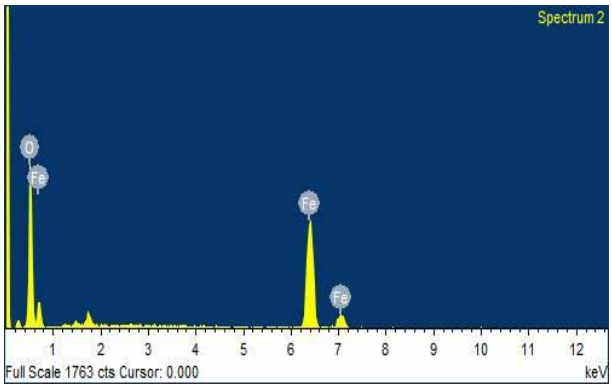
T a b l e 2

Chemical composition of goethite from Sivec by SEM-EDX (weight %)

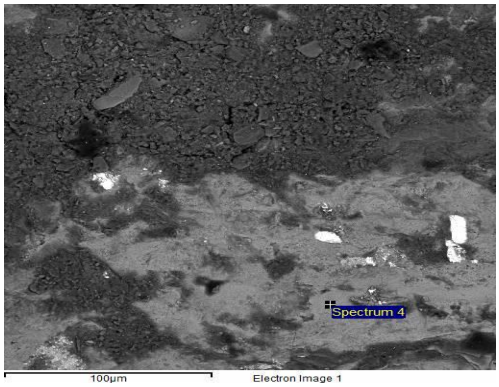
Element	Goethite from Sivec				Goethite from El Paso Co., Colorado, USA. Deer, et al., (1962)
	Analysis				
	1	2	3	4	
O	39.00	39.45	39.80	36.56	36.01
Fe	61.00	59.53	60.20	63.44	62.85
Cu	–	1.01	–	–	–
H	–	–	–	–	1.13
Total	100.00	100.00	100.00	100.00	100.00



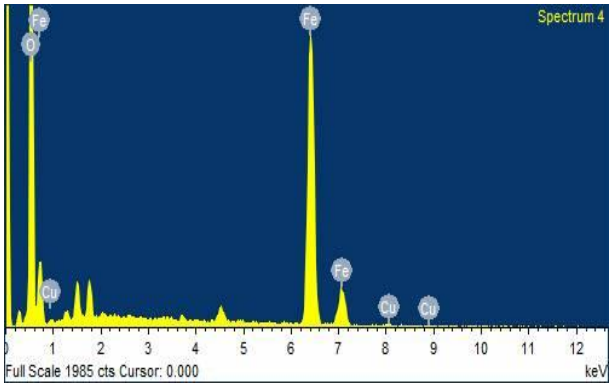
a) SEM image of goethite (analysis 1)



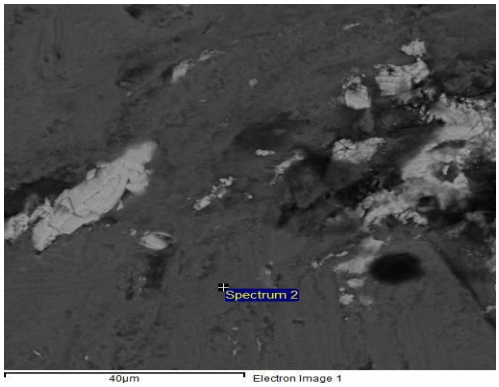
b) EDX spectrum of goethite (analysis 1)



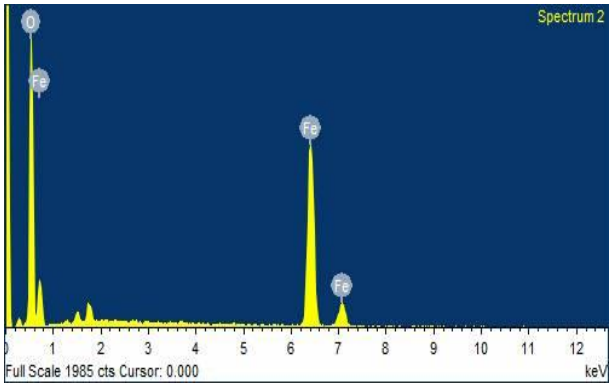
c) SEM image of goethite (analysis 2)



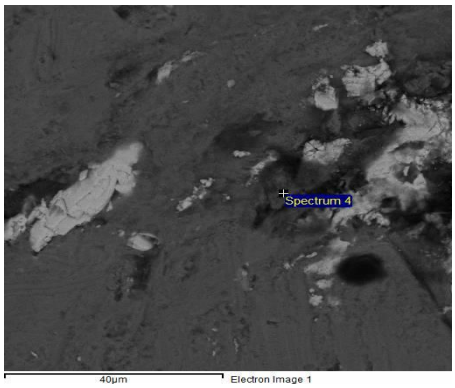
d) EDX spectrum of goethite (analysis 2)



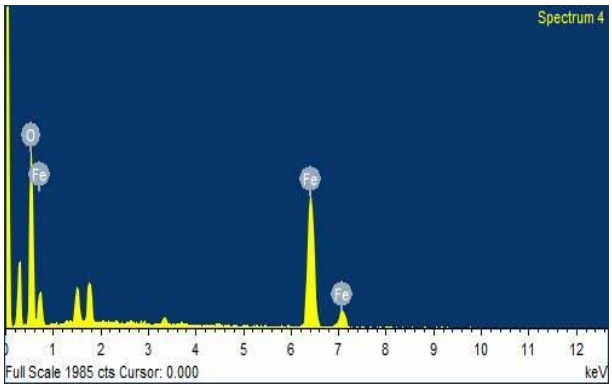
e) SEM image of goethite (analysis 3)



f) EDX spectrum of goethite (analysis 3)

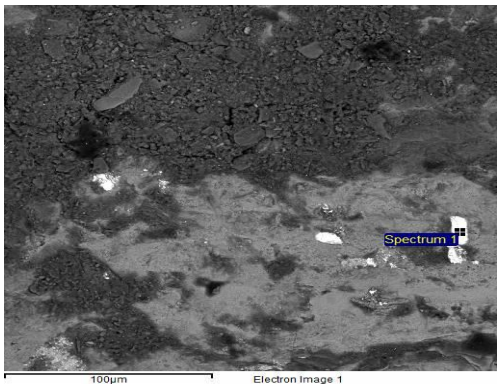


g) SEM image of goethite (analysis 4)

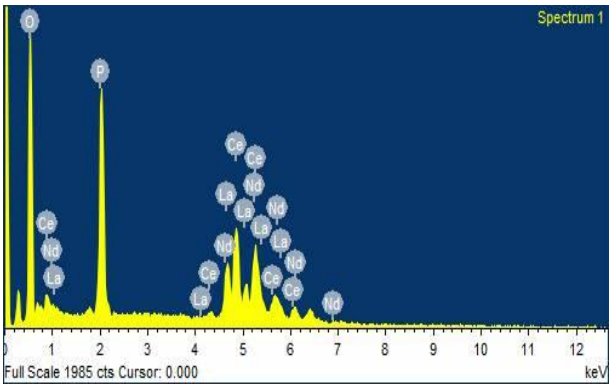


h) EDX spectrum of goethite (analysis 4)

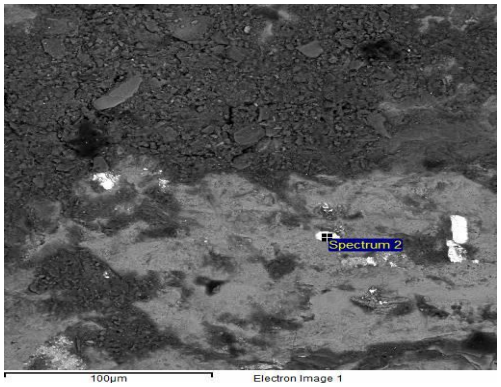
Fig. 4. SEM image and EDX spectrum of goethite from Sivec



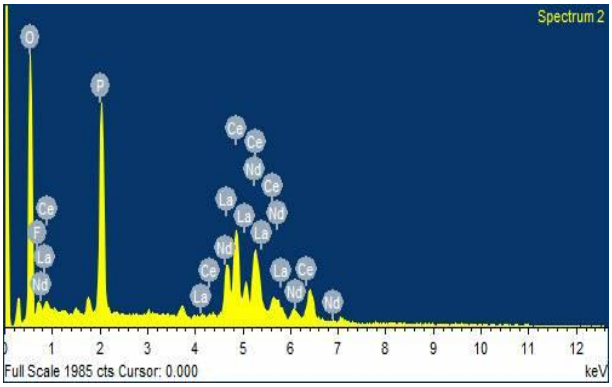
a) SEM image of monazite (analysis 1)



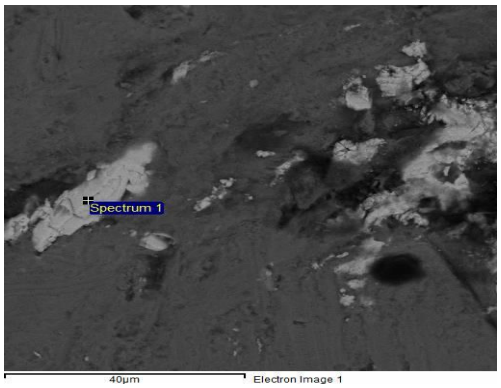
b) EDX spectrum of monazite (analysis 1)



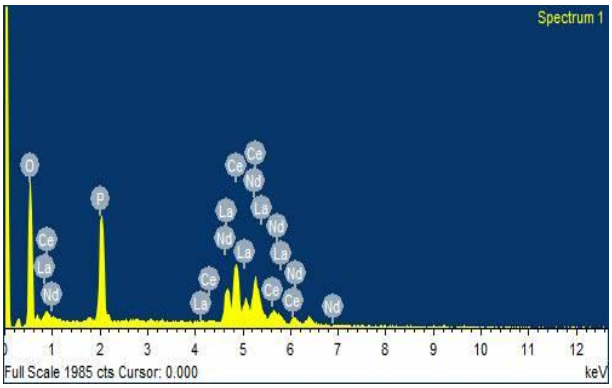
c) SEM image of monazite (analysis 2)



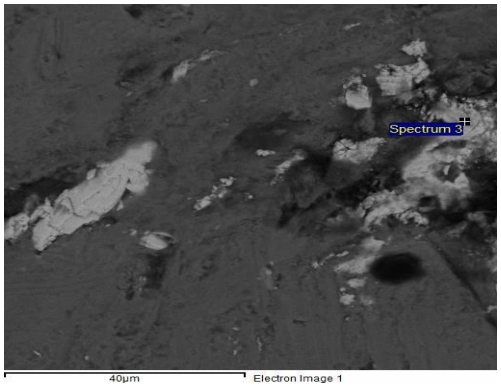
d) EDX spectrum of monazite (analysis 2)



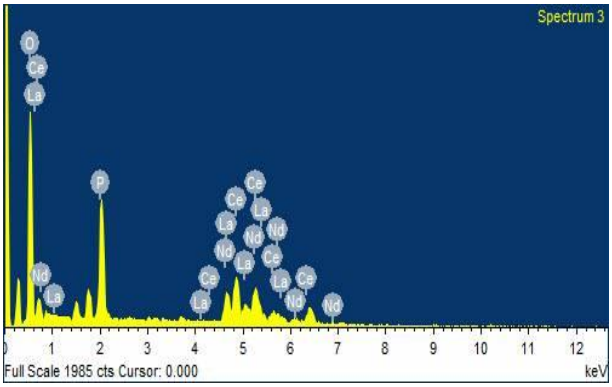
e) SEM image of monazite (analysis 3)



f) EDX spectrum of monazite (analysis 3)



g) SEM image of monazite (analysis 4)



h) EDX spectrum of monazite (analysis 4)

Fig. 5. SEM image of monazite and EDX spectrum of monazite from Sivec

T a b l e 3

Chemical composition of monazite from Sivec by SEM-EDX (weight %)

Element	Monazite from Sivec Analysis 1	2	3	4	Monazite from Mars Hill, Madison County, North Carolina (Palache et al., 1951)
O	31.30	32.92	28.66	40.05	26.64
P	14.01	14.05	12.56	13.58	12.89
La	16.16	15.80	18.39	14.80	14.46
Ce	27.87	27.13	31.76	24.38	29.17
Nd	9.67	10.10	8.63	7.20	12.01
F	0.99	–	–	–	–
Total	100.00	100.00	100.00	100.00	100.00

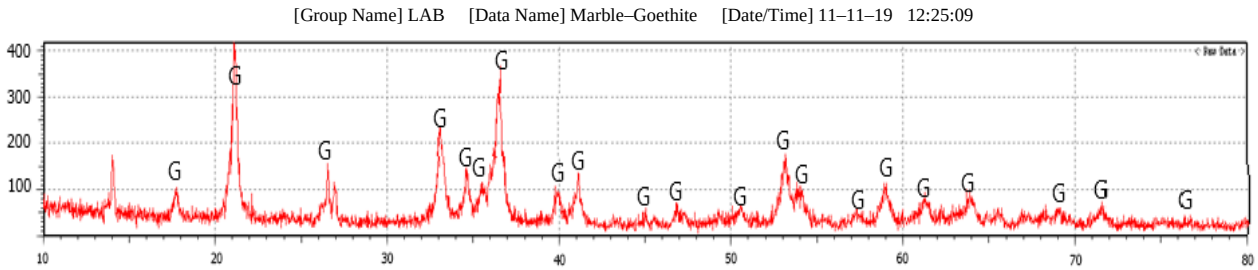


Fig. 6. XRD pattern of the investigated goethite from Sivec

CONCLUSION

This study describes the occurrence of goethite and monazite in the marble mass from Sivec for the first time. Goethite occurs in single crystals that occurred from the alteration of pyrite and it is found generally in the fine-grained parts of the white dolomitic marble. Pseudomorph of goethite has completely replaced pyrite from the matrix. The oxidation of iron sulfides invariably leads to the formation of goethite [α-FeO(OH)] in intimate association with the sulfides. The size of the goethite crystals is 1 cm. The color ranges from yellow – brown to nearly black. On the surface of the goethite crystal, small monazite crystals are found. The size of the monazite crystals varies in length 21.88 – 53.61 μm and width 8.45 – 20.38 μm.

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Р е з и м е

ПРЕЛИМИНАРНИ ИСТРАЖУВАЊА НА ГЕТИТ И МОНАЦИТ ОД СИВЕЦ, РЕПУБЛИКА СЕВЕРНА МАКЕДОНИЈА

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Во овој труд се презентираат резултати од прелиминарните истражувања на кристали на гетит кој се појавува во мермерите од Сивец. Испитаниот примерок беше анализиран со методите IR, SEM-EDS и XRD. Гетитот се јавува во мали кристали псевдоморфи по пирит, кои се наоѓаат главно во фино зрнести делови на белиот доломитски мермер. Кристалите се јавуваат поединечно. Бојата се движи од светло-кафеава до речиси црна, а сјајноста варира од земјена до полуметалична. Цепливоста е совршена по {010} и слабо совршена по {100}. Бојата на огребот е жолтеникаво кафеава. Големината на кристалот е 1 cm. Добиените податоци од рендгенските дифракциони испитувања се споредени со соодветните максимуми од дијаграмот на гетит, ICDD 00 017 0536. Со добиените податоци од рендгенските дифракциони испитувања се пресметани димензиите на елементарната ќелија. Добиени се следниве резултати: a = 4,617 Å, b = 9,976 Å, c = 3,024 Å, Z = 4, V = 139,32 Å^{3}. Со скенирачка електронска микроскопија беше утврдено и присуство на кристали на монацит. Кристалите на монацит се наоѓат на површината на кристалот на гетитот. Големината на кристалите на монацит варира во должина (21,88 –53,61 μm) и ширина (8,45 – 20,38 μm). Оваа студија за првпат ја опишува појавата на гетит и монацит во мермерната маса од Сивец..