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Characteristics of minerals in Slovenian marbles

Značilnosti mineralov v slovenskih marmorjih

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Abstract

Common rock-forming and accessory minerals in marbles from various localities in Slovenia were studied using scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). Minerals and their chemical composition were identified in order to verify the variability of mineral assemblages in marbles from different localities in Slovenia. The analysis showed that marbles from Košenjak are the most mineralogically diverse, followed by Pohorje and finally Strojna marbles. Common rock-forming minerals calcite and dolomite are more abundant in Pohorje marbles where calcite contains higher levels of magnesium but no strontium and iron as compared with Strojna and Košenjak marbles. Accessory minerals like quartz, mica, titanite, apatite, rutile, zircon, chlorite group minerals, kaolinite and iron oxides/hydroxides were found in marbles from all localities. Clinopyroxene, amphibole, epidote and smectite group minerals, talc, tungsten-bearing ilmenorutile, psilomelane and bismuth oxides/carbonates, were observed only in marbles from Pohorje, while tourmaline and allanite group minerals, thorite or huttonite, chalcopyrite and synchysite group minerals were detected in marbles from Košenjak and Strojna. Variations in mineral assemblages in marbles from different locations are likely a consequence of different sedimentary environment and conditions and metamorphic grade of marble. These differences indicate that marbles from Košenjak and Strojna are genetically different from those from Pohorje and probably reflect mineral composition of the protolith. Thus, they enable rough distinction between more distant locations, but not between individual sub-localities.

Izvleček

Z vrstično elektronsko mikroskopijo, z energijsko disperzijsko spektroskopijo (SEM/EDS) smo raziskali kamninotvorne in akcesorne minerale v marmorjih z različnih lokacij v Sloveniji. Opredeljeni so bili minerali in njihova kemična sestava z namenom oceniti variabilnost mineralnih združb v marmorjih. Analiza je pokazala, da so marmorji s Košenjaka mineraloško najbolj raznoliki, sledijo pohorski marmorji in marmor s Strojne. Kamninotvorna minerala kalcit in dolomit sta v največjih količinah prisotna v pohorskih marmorjih, v katerih ima kalcit višje vsebnosti magnezija kot kalcit v marmorjih s Košenjaka in Strojne, vendar ne vsebuje železa in stroncija. Akcesorni minerali, kot so kremen, sljuda, titanit, apatit, rutil, cirkon, minerali kloritne skupine, kaolinit in železovi oksidi/hidroksidi, so prisotni v marmorjih z vseh lokacij. Klinopiroksen, minerali amfibolove, epidotove in smektitne skupine, lojevec, ilmenorutil z volframom, kromit, psilomelan in bizmutovi oksidi/karbonati so bili prisotni samo v pohorskih marmorjih, medtem ko so bili minerali turmalinove in allanitove skupine, torit ali huttonit, halkopirit in minerali sinhisitove skupine prepoznani le v marmorjih s Košenjaka in Strojne. Ugotovljene so bile razlike v mineralnih združbah v marmorjih z različnih lokacij, ki so verjetno posledica različnega sedimentacijskega okolja in pogojev ter različne stopnje metamorfoze marmorjev. Te razlike kažejo, da so marmorji s Košenjaka in Strojne genetsko drugačni od tistih s Pohorja in verjetno odražajo mineralno sestavo protolita. Tako omogočajo grobo razlikovanje med bolj oddaljenimi lokacijami, vendar ne med mikrolokacijami znotraj posameznih lokacij.

Introduction

Marble is a metamorphic rock composed mostly of carbonate minerals, generally calcite prevailing over dolomite. Despite its carbonate-rich character (Blatt & Tracy, 1999), marble contains various amounts of other noncarbonate minerals, especially silicates and oxides. The variety of noncarbonate minerals is derived by abundance of the original detrital minerals in the limestone and dolostone and their reactions with carbonates during metamorphism (Blatt & Tracy, 1999). Depending on the metamorphic grade the common noncarbonate minerals are dominated by quartz, brucite, phlogopite, chlorite group minerals, tremolite, diopside, forsterite, wollastonite, grossular, Ca-rich plagioclase and vesuvianite (Blatt & Tracy, 1999; Best, 2007). Therefore, the presence of noncarbonate minerals could provide information on chemistry and mineralogy of the protolith, and even the temperature and pressure during the process of metamorphism (Blatt & Tracy, 1999; Best, 2007). Hence, they are important tracers of the source areas of marble.

In Slovenia, there are several marble outcrops on Pohorje, Strojna and Košenjak – western Kozjak (Mioč, 1978; Mioč, 1983; Mioč & Žnidarčič, 1989). In the past, much attention was given to metamorphic rocks from Pohorje Mts. (Germovšek, 1954; Hinterlechner-Ravnik, 1971, 1973; Janák et al., 2004, 2005, 2006, 2009, 2015; Jarc & Zupančič, 2009; Jarc et al., 2010; Jeršek et al., 2013; Mrvar, 2013; Vrabec et al., 2010a, b; Vrabec et al., 2018). Here, the majority of medium to high-grade marbles are located in the eastern and southern parts of the massif between Oplotnica and Dravinja brooks and in the surroundings of Šmartno, where they are placed among gneisses, mica-schists and amphibolites (Hinterlechner-Ravnik & Moine, 1977; Mioč, 1978). Calcite marbles dominate, but dolomite-containing marbles are also present. The marbles are coarse-grained to less often fine-grained with granoblastic texture (Hinterlechner-Ravnik, 1971, 1973; Hinterlechner-Ravnik & Moine, 1977). Common accessory minerals are quartz, Na-rich plagioclase, tremolite, hornblende, diospide, mica, while garnet (mostly almandine), graphite, pyrite and chlorite, epidote, clinozoisite and serpentine group minerals occur rarely (Hinterlechner-Ravnik, 1971). Besides these, titanite, ferric oxides, vesuvianite, scapolite (Jarc & Zupančič, 2009; Jeršek et al., 2013), zircon, rutile and zoisite (Mrvar, 2013) have been found. Accessory minerals occur in bands, and are more frequent on the edges of marble lenses (Mrvar, 2013). Marble outcrops are small, with the exception of Rimski kamnolom in Bistriški Vintgar which has a size of about 15m × 100m (Mrvar, 2013).

Low to medium-grade marbles from western Kozjak Mts. are bluish-greyish and laminated with the high content of accessory minerals such as quartz, plagioclases, zoisite-epidote with fragments of felsic composition and phyllite (Hinterlechner-Ravnik, 1973). Several meters thick layers and small lenses of marble in Košenjak are intercalated between gneisses and mica-schist. Marbles are granoblastic, middle to coarse grained (Mioč, 1978). On Strojna, there are small outcrops of 20 cm to 50 cm thick low-grade marbles (Mioč, 1983). They contain a lot of non-carbonate minerals (e.g. quartz; Mioč, 1983).

The SEM/EDS analysis enables detection of smaller accessory minerals, which have not been reported yet, and assessment of their chemical composition. The aim of this study was therefore to characterise the accessory minerals in the marbles from different Slovenian localities by SEM/EDS analysis and to verify the local variability of the mineral assemblages and their mineral chemistry.

Geological setting

The Pohorje Mts., Strojna and Kozjak Mts. constitute the most south-eastern part of the Eastern Alps. Eastern Alps consist of a system of large nappes named Austroalpine of Cretaceous age that formed during the Eoalpine orogeny (Frank, 1987; Schmidt et al., 2004; Fodor et al., 2008). Pohorje nappe is the deepest tectonic unit (Janák et al., 2004; 2006), mainly composed of medium- to high-grade metamorphic rocks, e.g. gneisses and mica schists with lenses of amphibolite, quartzite, marble and eclogite, and north from Slovenska Bistrica also ultramafic body (SBUC) (Janák et al., 2006).

The Pohorje nappe is overlain by the nappe of weakly metamorphosed Paleozoic rocks, mainly low-grade metamorphic slates and phyllites (Hinterlechner-Ravnik, 1971, 1973; Vrabec, 2010b). The upper-most nappe is built up of Permo-Triassic clastic sedimentary rocks, prevailingly sandstones and conglomerates (Hinterlechner-Ravnik, 1971, 1973; Janák et al., 2004; Vrabec, 2010b). The entire nappe stack is overlain by early Miocene sediments, which belong to the syn-rift basin fill of the Pannonian Basin (Fodor et al., 2003). A large granodiorite body with dacite intruded in Miocene in the central part of the Pohorje massif (Dolar Mantuani, 1935; Faninger, 1970; Zupančič, 1994a, b, Trajanova et al., 2008).

In the Pohorje Mts. area, the regional metamorphism under ultra-high pressures and temperatures took place (Hinterlechner-Ravnik, 1971; Vrabec et al., 2012; Janák et al., 2015) during the Cretaceous Eo-Alpine Orogeny (Thony, 2002; Miller et al., 2005).

The Pohorje Mts., Strojna and Kozjak Mts. have very similar lithology and structure. The Strojna is separated from Pohorje Mts. by the Labot fault and the Periadriatic fault system (Mioč, 1978; Mioč & Žnidarčič, 1989). On the southern side, the Košenjak (western Kozjak) is separated from the Pohorje Mts. by the mid-Miocene Ribnica trough (Mioč, 1978).

Materials and methods

Sampling and sample preparation

A total of 24 samples of marble were collected from larger and smaller outcrops (Fig. 1). Since marble occurrences are more frequent on Pohorje Mts. and in order to check the spatial mineralogical diversity of the marble, 13 samples were taken from five different Pohorje locations, which include Hudinja (north from Vitanje; three samples), a Roman quarry Rimski kamnolom, one of the largest marble outcrops (in Bistriški vintgar; three samples), Bojtina (two samples), a smaller outcrop in Zgornja Nova Vas (three samples), and Črešnova (north from Zreče; two samples). On Strojna, four samples were taken from two small (app. 2 × 2-3 m) outcrops, and on Kozjak (Košenjak), five samples were collected along local road in the vicinity of state border and two samples from the larger up to 20 m high outcrops near border crossing Muta. From all samples, polished thin sections were prepared for inspection with scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS).

SEM/EDS analyses

SEM/EDS analysis was carried out at the Geological Survey of Slovenia using a JEOL JSM 6490LV SEM coupled with an Oxford Instruments INCA Energy 350 EDS, at an accelerating voltage of 20 kV, spot size 50 and a working distance of 10 mm. The polished thin sections were carbon-coated and analysed in backscattered electron (BSE) mode under high vacuum. The chemical composition of individual minerals was measured using EDS point analysis with acquisition time of 60 s. X-ray spectra were optimised and calibrated for quantification using pre-measured standards included in the EDS software, which is a basic standardisation procedure in fitted-standards EDS analysis (Goldstein et al., 2003), referenced to a Co optimisation standard. Based on the standard ZAF-correction

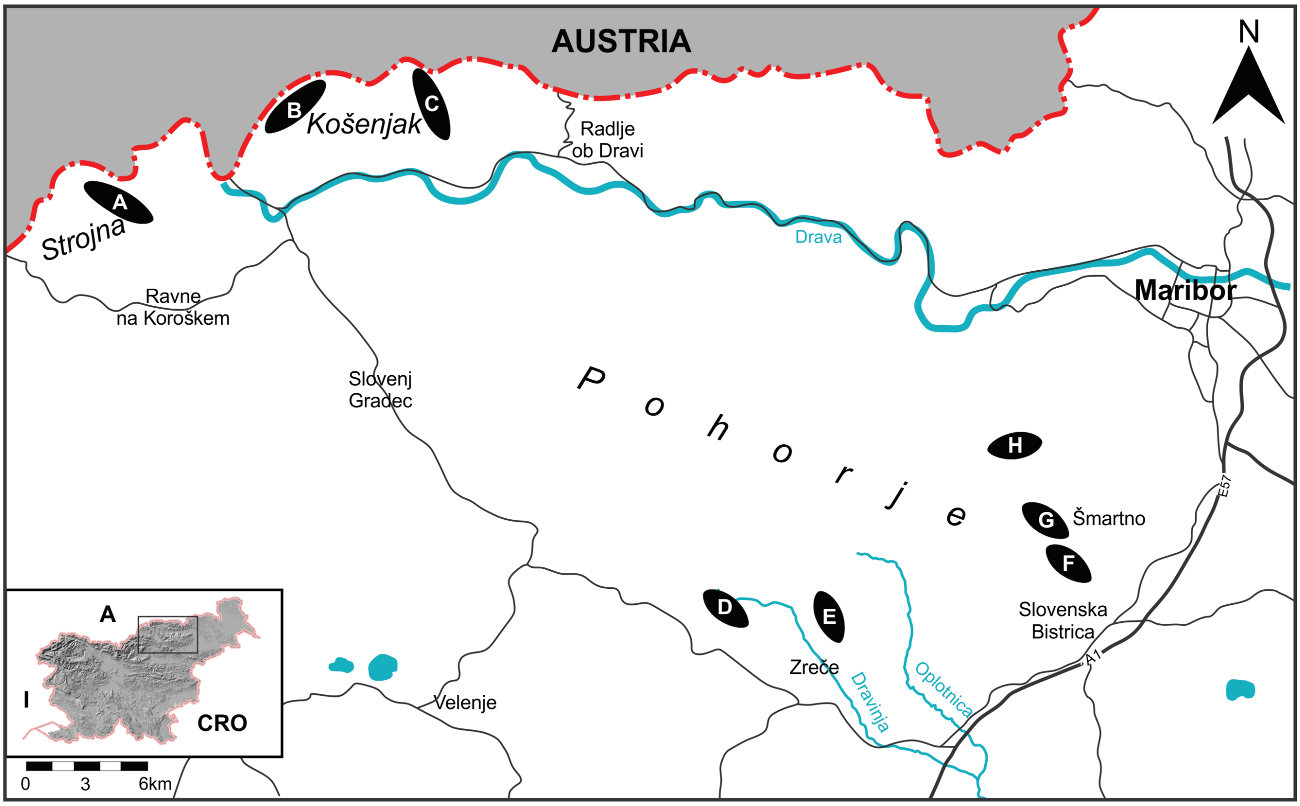

Fig. 1. Sampling locations (A – Strojna; B, C – Kozjak Mts. (Košenjak); D, E, F, G, H – Pohorje Mts. (D – Hudinja, E – Črešnova, F – Rimski kamnolom, G – Zgornja Nova Vas, H – Bojtina)).

procedure included in the INCA Energy software (Oxford Instruments, 2006), the correction of EDS data was performed. In order to assure good quality of the EDS results, only data with deviation <10 wt.% were considered for identification of minerals. Minerals were assessed by calculating stoichiometric ratios from at.% of constituent elements, acquired by the EDS analysis and comparison with atomic proportions of constituent elements in known stoichiometric minerals, obtained from mineral databases (Wünsch, 2001; Anthony et al., 2009; Barthelmy, 2010) and EDS spectra (Welton, 1984; Severin, 2004; Reed, 2005). Mineral formulae of selected minerals were obtained from mineral databases (Wünsch, 2001; Anthony et al., 2009; Barthelmy, 2010).

Results and discussion

The SEM/EDS analyses showed that calcite marbles prevail, but minor amount of dolomite is also present in samples from Pohorje. Although the focus of the study was determination of accessory minerals, the relative abundances of calcium and magnesium carbonates (calcite, dolomite) and elemental composition of calcites were also measured. The list of the identified accessory minerals or mineral groups is summarised in Table 1.

Common rock-forming minerals - calcite and dolomite

In general, marbles from Košenjak and Strojna contain between 70 to 85 % and 75 to 95 % carbonates (between 5 to 30 % noncarbonate minerals), respectively, whereas Pohorje marbles consist of 95 to 97 % of carbonates (up to 5 % of noncarbonate minerals). This indicates that Pohorje marbles are purer and appear to contain fewer accessory minerals.

Calcite in studied marbles is relatively pure, however it contains some magnesium, iron and strontium, which commonly substitute for calcium in calcite (Chang et al., 1998). Minor content of magnesium in calcite was detected in samples from all locations, with the exception of Bojtina samples. Nevertheless, calcite in Pohorje marbles contains somewhat higher levels of magnesium (mean of 0.42 at.%) compared with that in marbles from Košenjak (mean of 0.20 at.%) and Strojna (mean of 0.11 at.%). Iron in calcite was detected only in marble samples from Košenjak and Strojna. Strontium in calcite was found in all samples from Košenjak and Strojna, while it was not detected in samples from Pohorje. Presence of strontium is in agreement with marine aragonite (Fairbridge, 1967) but may also reflect different carbonate depositional environments. Since calcium/strontium ratio in calcium carbonate does not change during metamorphism (Lazzarini, 2004), and strontium is reported to be relatively immobile at high metamorphic grades (De Vos et al., 2006), and since high strontium contents have already been observed in high-grade marbles (Ofotfjorden area, Norway) whose origin was attributed to aragonitic protolith (Melezhik et al., 2003; 2013), strontium content in studied marbles probably reflects different sedimentary environment and diagenesis and metamorphic evolution. Therefore, we can assume that marbles from Košenjak and Strojna are genetically different from those from Pohorje. This finding is in agreement with findings of Jeršek et al. (2013) that Pohorje marble was metamorphosed from calcite prevailing protolith. Presence or absence of strontium could thus be used to distinguish marbles from Pohorje Mts. area from other localities.

Accessory minerals

The study showed that marbles from Pohorje, despite their higher carbonate content, seem to be mineralogically as diverse as marbles from other two localities. However, the number of different minerals or mineral groups at each specific location in Pohorje area is generally significantly smaller (Table 1). This could be explained by the higher number of analysed samples from this area, scattered sampling locations and the fact that Pohorje marbles are highly heterogeneous in isotopic and geochemical parameters as well as grain sizes (Jarc et al., 2010). Taking this into consideration, the highest number of identified minerals or mineral groups is found in marbles from Košenjak – beside calcite we identified 27 accessory minerals (Table 1). On the other hand, marble from Črešnova shows the lowest diversity in accessory minerals – only 10 of them have been observed (Table 1).

Quartz, muscovite (some grains have elevated barium content), titanite, apatite, rutile, zircon, chlorite group minerals, kaolinite and iron oxides/hydroxides are very common and have been found in samples from all localities (Table 1). SEM/EDS analyses revealed differences in chemical compositions of some very common accessory minerals, titanite and apatite. It seems that the elemental composition of titanites depends on the sampling locations, as in Košenjak and Strojna marbles they have higher contents of aluminium and fluorine incorporated in their crystal structure than those in Pohorje marbles.

Table 1. Mean number of identified accessory mineral grains in number (n) of samples from studied localities/locations

Mineral/mineral group	**Sampling locality**			**Pohorje (PO) sampling locations**				
	ST(A)	**KO(B, C)**	**PO**	**HU(D)**	**CR(E)**	**RK(F)**	**ZNV(G)**	**BO(H)**
	n=4	**n=7**	**n=13**	**n=3**	**n=2**	**n=3**	**n=3**	**n=2**
Actinolite			1.2			4.7		0.5
Alkali feldspar	0.3		0.3				1.3	
Allanite group	0.3	1.6						
Alloclasite/cobaltite		0.1						
Apatite group	3.5	2.0	2.2	1.3	3.0	2.0	2.0	3.0
Asbolane	0.3							
Ba-muscovite	3.0	0.9	0.4	1.7				
Bastnäsite	0.3							
Bismuth/bismite/bismutite			0.1			0.3		
Chalcopyrite	0.3	0.3						
Chlorite group	0.3	0.4	1.4	3.7		1.0		2.0
Diopside			0.5			0.7		2.0
Epidote			0.2					1.5
Fe-oxide/hydroxide	2.0	0.7	0.2	0.3		0.3	0.3	
Fluorite		0.4						
Galena		0.4						
Hornblende			0.2			1.0		
Ilmenorutile (W)			0.1			0.3		
Kaolinite	2.8	0.9	0.3		2.0			
Molybdenite		0.6						
Monazite group	0.3							
Muscovite	2.8	3.0	0.6	0.3			1.0	2.0
Phlogopite		0.4	1.5	1.7		3.0	1.7	
Plagioclase		2.4	0.8	1.3		0.3		2.5
Psilomelane			0.2				0.7	
Pyrite		2.4	0.7	0.7	0.5	1.7		0.5
Pyrrhotite		2.1	0.5		1.0	1.0		1.0
Quartz	3.8	3.1	2.2	3.7	1.5	0.3	1.3	5
Rutile	1.5	1.0	0.6	0.3	0.5	1.3	0.3	0.5
Smectite group			0.5				2.3	
Sphalerite		0.1	0.2		0.5	0.3		
Synchysite group/petersenite	0.3	0.3						
Talc			0.7	1.0	1.5	1.0		
Thorite/huttonite	0.8	0.1						
Titanite	0.5	3.7	1.5	1.7	1.0	1.3	1.0	2.5
Tourmaline group	1.0	0.3						
Ullmannite		0.1						
Uraninite		0.3	0.2			0.7		
Zircon	1.0	1.9	0.5	0.3		0.3	0.3	1.5
Zoisite		1.3	0.5	0.7	0.5			1.5
∑ mean number of grains	24.6	31.0	18.1	18.7	12.0	21.7	12.3	26.0
Number of mineral species	18	27	27	14	10	19	11	14

ST-Strojna, KO-Košenjak, PO-Pohorje (HU-Hudinja, CR-Črešnova, RK-Rimski kamnolom, ZNV-Zgornja Nova Vas, BO-Bojtina)

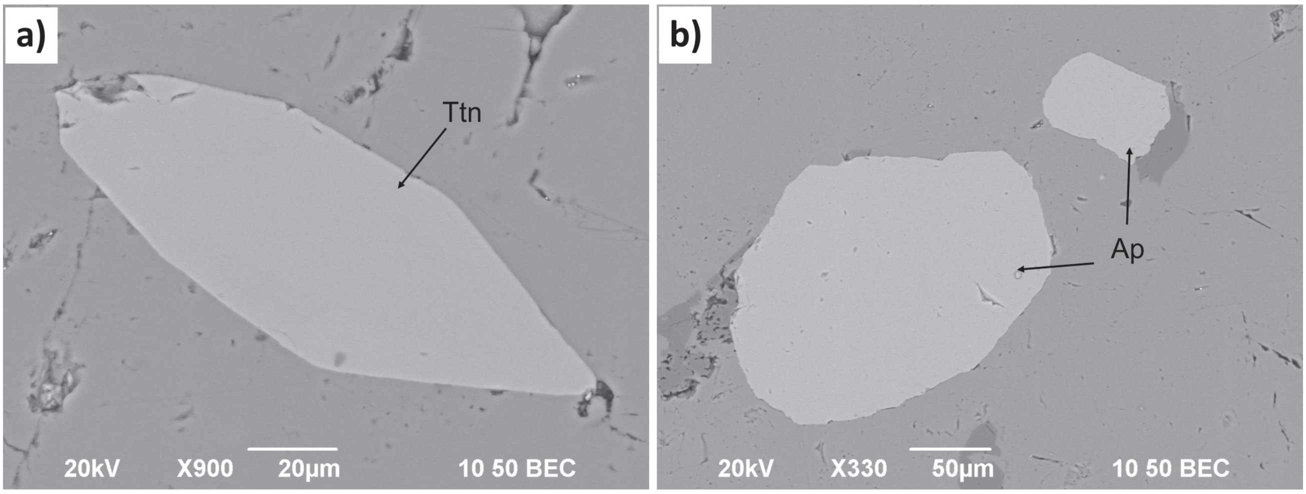

Fig. 2. SEM (BSE) images of: a) titanite (Ttn) grain in marble from Hudinja; b) apatite (Ap) grains in marble from Hudinja.

In all samples, titanite occurs mostly as euhedral individual grains (Fig. 2a) in calcite or is associated with other minerals. In samples from Košenjak, titanite is associated with plagioclase, muscovite, Ba-muscovite, zoisite, fluorapatite, uraninite and also zircon, which occurs as an inclusion in some titanite grains. In samples from Strojna, titanite was found associated with muscovite. Titanites in samples from Hudinja, Rimski kamnolom and Zgornja Nova Vas are associated with zoisite and anorthite, phlogopite and actinolite, and quartz, respectively. The mean sizes of titanite grains are 100 µm in Košenjak samples and 62 µm in Strojna samples, while in the samples from Pohorje they range from 71 µm in Črešnova to 116 µm in Rimski kamnolom samples.

Rutile, which was found in all samples (Table 1), is mostly associated with titanite. Individual euhedral grains in calcite are rarely found. By its chemical composition, rutile is mostly pure, however in samples from Košenjak and Strojna rutile grains have minor contents of vanadium and iron. It can be assumed that rutile is mostly a secondary mineral formed during metamorphism, however individual grains in calcite could also originate from the protolith. The sizes of rutile grains are up to 25 µm in Košenjak samples, up to 68 µm in Strojna samples. In the Pohorje samples they range from 5 µm in Črešnova to 35 µm in Bojtina samples.

Apatite is also found in samples from all localities (Table 1). All measured apatite grains contain fluorine, whose content depends on the location. Apatite in marble samples from Košenjak and Strojna has higher fluorine contents than those in Pohorje marbles, while those in Pohorje marbles has also minor content of chlorine. Apatite mainly forms euhedral rounded to elongated grains with isometric cross-sections (Fig. 2b) as individual grains in calcite or in association with other minerals. In samples from Košenjak, it is associated with phlogopite, plagioclase (albite and oligoclase), muscovite and quartz. Apatite in samples from Strojna is associated with iron oxides/hydroxides. In samples from Hudinja and Rimski kamnolom, it is accompanied by dolomite, while in Zgornja Nova Vas and Bojtina samples apatite is associated with muscovite and plagioclase, respectively. The mean sizes of apatite grains are 106 µm in Košenjak samples and 85 µm in Strojna samples, while in the samples from Pohorje they range from 76 µm in Zgornja Nova Vas to 231 µm in Hudinja samples.

Tourmaline and allanite group minerals, thorite or huttonite, chalcopyrite and minerals of synchysite group ($Ca(Ce,La)(CO_3)_2F$), or pseudomorphs of synchysite after petersenite ($(Na,Ca)_4(Ce,La,Nd,Sr)_2(CO_3)_5$), were detected in samples from Košenjak and Strojna, but not in Pohorje marbles. Tourmaline grains with composition of uvite or dravite are euhedral, zoned and up to 200 µm in size. They are associated with rutile and illite. Grains of allanite group minerals are zoned, anhedral and up to 70 µm large. They occur individually in calcite or accompany quartz and pyrite. Anhedral chalcopyrite grains of 50 µm in size form assemblages with pyrite and muscovite in Košenjak marbles and with kaolinite and rutile in Strojna marbles. Plagioclase, phlogopite, zoisite, pyrite, pyrrhotite, sphalerite and uraninite were observed in marbles from Košenjak and Pohorje. Compositions of plagioclase vary from albite to anorthite. Anorthite was present particularly in Košenjak and Hudinja samples. In some samples (Strojna and Pohorje), alkali feldspar (e.g. anorthoclase) is present (Table 1). Phlogopite occurs as subhedral (in Košenjak) to anhedral (in Pohorje samples) flakes with elongated cross-sections with size of up to 550 µm. Phlogopite forms assemblages with apatite and titanite in Košenjak and with talc, dolomite, chlorite group minerals and illite in Pohorje marbles. Zoisite is up to 200 µm large in all marbles. In Košenjak marbles it is elongated and subhedral and associated with quartz, titanite and pyrite, while in Pohorje marbles it is anhedral and found as inclusions in plagioclase or kaolinite grains. In some grains of zoisite in Košenjak samples, minor content of strontium was detected. Some pyrite grains in Košenjak samples contain minor level of nickel, while some pyrites from Pohorje (Rimski kamnolom) samples contain either minor level of cobalt or arsenic. Also, some pyrrhotite grains in Košenjak and Pohorje (Rimski kamnolom, Bojtina) samples contain minor level of nickel. Pyrite and pyrrhotite commonly form assemblages with other sulphides. Sphalerite is subhedral with isometric cross-sections and up to 34 µm large and forms assemblages with pyrrhotite, pyrite with molybdenite inclusion and quartz.

Some minerals were found only in marbles of a specific metamorphic grade and from a specific location, which could be a consequence of different sedimentary environment and conditions and/or degree of metamorphism. Thus, anhedral void-filling fluorite, galena (subhedral inclusions in pyrite and pyrrhotite), molybdenite (also with minor content of tungsten), ullmannite (NiSbS) and ((Co,Fe)AsS) or cobaltite (CoAsS) were found only in marbles from Košenjak, while monazite group minerals (subhedral grains in calcite), bastnäsite ($(Ce,La)(CO_3)F$) and asbolane ($(Ni,Co)_xMn(O,OH)_4 \cdot nH_2O$) are present only in Strojna marbles. Clinopyroxene (e.g. diopside, augite) (anhedral and associated with actinolite), amphibole (hornblende, actinolite) (subhedral to anhedral and associated with pyrite, apatite, titanite, dolomite) and epidote group minerals (euhedral in assemblage with chlorite group minerals and quartz), talc (elongated anhedral and associated with phlogopite, chlorite group minerals and dolomite), smectite group minerals, tungsten-bearing ilmenorutile ($(Ti,Nb,Fe)O_2$), psilomelane (anhedral fillings in chlorite group minerals and quartz or euhedral needle-like crystals along cleavage planes in dolomite) and bismuth oxides or carbonates were observed only in Pohorje marbles. This could also result from highly variable mineral composition of marbles and the relatively small number of inspected samples. For example, epidote was observed only in samples from Bojtina, but other researchers detected it also in marbles from other localities on Pohorje (Jarc & Zupančič, 2009; Jarc et al., 2010; Jeršek et al., 2013) and Košenjak (Komar, 2006). Diopside was also previously found in Bojtina (Jeršek et al., 2013), in the surroundings of Črešnova (Hinterlechner-Ravnik, 1971) and Slovenska Bistrica (Mrvar, 2013). This shows that the marbles are very heterogeneous, also regarding content and type of accessory minerals.

The mineral assemblages of index minerals, which indicate the degree of metamorphism according to Blatt & Tracy (1999), are similar in all studied marbles and show similar metamorphic grades (Table 1). However, the greatest amount of minerals typical of low metamorphic grades (e.g. muscovite, chlorite group, rutile, albite) was found in Košenjak and Strojna marbles. Minerals of medium metamorphic grades (e.g. titanite, epidote, hornblende, diopside) are most abundant in Košenjak marbles, while minerals indicating high metamorphic grades (e.g. zoisite, alkali feldspar, phlogopite) prevail in Pohorje marbles. This is consistent with high-grade metamorphic rocks of Pohorje Mts. (Hinterlechner-Ravnik, 1971; Vrabec et al., 2012; Janák et al., 2015) and with low metamorphic grades reported for Strojna marbles (Mioč, 1983).

Some minerals described in this study have been observed for the first time in Slovenian marbles. These minerals are synchysite group minerals or pseudomorphs of synchysite after petersenite, bastnäsite, tungsten-bearing ilmenorutile, ullmannite, asbolane, alloclasite or cobaltite, bismuth/bismuth oxides or carbonates, thorite or huttonite, uraninite and molybdenite. Synchysite group minerals, or pseudomorphs of synchysite after petersenite, occur as up to 40 µm large anhedral aggregates of fibrous crystals in kaolinite (Fig. 3a), which are in Strojna samples associated with 29 µm large anhedral grains possibly of mineral bastnäsite. Synchysite fibrous crystals can also be found along cracks in grains of allanite group minerals or along the calcite-mica boundaries. Both synchysite and bastnäsite are possibly secondary minerals that could have formed due to local hydrothermal activity. Synchysite has already been found in low-grade high REE-marbles within biotite phyllites of Horní Dunajovice in Western Moravia, where REE enrichment was ascribed to protolith composition and formation of synchysite to early metamorphosis (Houzar et al., 2004). Others reported synchysite in high-grade marbles, e.g. in Otter Lake area (Quebec), occurring as inclusions within fluorapatite together with some other rare accessory minerals, such as allanite and thorite (Martin et al., 2017). Bastnäsite was observed also in carbonatite related, altered dolomite marble in Bayan Obo (Mongolia) (Smith et al., 1999). Uraninite is mostly chemically pure, but some grains may also contain minor level of thorium. It forms euhedral to subhedral subrounded grains with sizes ranging between 3 μm and 16 μm and mostly isometric cross-sections. They are associated with about 6 μm large anhedral grain of tungsten-bearing ilmenorutile, pyrite (Fig. 3b) and titanite and only few grains are found individually in dolomite and calcite. Ullmannite occurs as euhedral to subhedral grain with size of about 5 μm associated with pyrrhotite (Fig. 3c). Ullmannite has been reported in medium to high-grade metamorphic metasedimentary rocks from hydrothermal solutions (Dobbe, 1991), but was also found in low-grade dolomite marbles in Watten valley (Austria) (Haditsch & Mostler, 1983). Asbolane is up to 12 μm large anhedral and plumose aggregates of fibrous crystals filling voids and cracks at the contact between mica and calcite (Fig. 3d). Its morphology and form of occurrence indicate that it is a secondary mineral. Alloclasite or cobaltite (Fig. 4a) forms a 4 μm large euhedral inclusion in pyrrhotite, which is associated with a grain of biotite group mineral. About 1 μm large elongated and subhedral inclusion of bismuth/bismuth oxide or carbonate (Fig. 4b) was found in pyrrhotite at the boundary with calcite. No reports on asbolane, alloclasite or cobaltite and bismuth/bismuth oxide or carbonate occurrences in marbles have been found. Thorite or huttonite occurs as euhedral to subhedral grains of 30 μm in size (Fig. 4c), mostly as inclusions in Ba-muscovite or in association with quartz, zircon and pyrite. Some grains appear to be intergrown with yttrialite. Ditz et al. (1990) reported thorite in metasomatised impure marbles near contacts of granitic and pegmatitic intrusions of Grenville subprovince (Canada), while Drábek et al. (2017) found thorite together with molybdenite, pyrite, pyrrhotite, galena and chalcopyrite also in regionally metamorphosed medium to high-grade carbonatite-like marble at Bližná. Molybdenite forms laths or tabular crystals with grain sizes ranging between 13 μm and 38 μm. They are mostly enclosed in pyrite or in mica (Fig. 4d) and quartz. Some molybdenite grains contain minor levels of tungsten. No reports on molybdenite in marbles have been found, however, lath-like tungsten rich molybdenite was found in granite rocks within orthogneiss at Vítkov (Bohemian Massif, Czech Republic) (Pašava et al., 2015).

Since these rare minerals occur in many different metamorphic rocks (including marbles) varying in metamorphic grade, they could not be considered as definite indicators of metamorphic grade.

Some minerals that were reported in the literature, such as garnet, graphite, serpentine group minerals (Hinterlechner-Ravnik, 1971), tremolite (Jarc & Zupančič, 2009; Mrvar, 2013), vesuvianite (Jeršek et al., 2013) and scapolite (Jeršek et al., 2013; Mrvar, 2013), were not observed in our study. This indicates the highly heterogeneous mineral assemblages in marbles from studied sites.

Conclusions

Marbles from Pohorje Mts. are relatively pure, composed mostly of carbonate and containing only up to 5 % of noncarbonate minerals, while marbles from Košenjak and Strojna localities contain from 5 % to 30 % of noncarbonate minerals.

Marbles from Košenjak are mineralogically the most diverse. Beside calcite, we recognized 27 minerals or mineral groups, while in marbles from Črešnova only 10 minerals or mineral groups besides calcite and dolomite were detected. Some minerals like quartz, mica, titanite, apatite, rutile, zircon, chlorite group minerals, kaolinite and iron oxides/hydroxides are very common and were found in marbles from all localities. Other minerals, such as clinopyroxene, amphibole, epidote, and smectite group minerals, talc, tungsten-bearing ilmenorutile, psilomelane and bismuth oxides or carbonates, were observed only in samples from Pohorje Mts., while tourmaline and allanite group minerals, thorite or huttonite, chalcopyrite and minerals of synchysite group, or pseudomorphs of synchysite after petersenite, were detected in marbles from Košenjak and Strojna.

Further, SEM/EDS analysis showed the differences in chemical composition of calcite, titanite and apatite in marbles from different localities. Namely, calcites in samples from Košenjak and Strojna contain detectable amounts of strontium, which is not detected in Pohorje samples. Titanites from Košenjak and Strojna contain higher level of aluminium and fluorine than those from Pohorje marbles. Apatite in marbles from Košenjak and Strojna has also higher content of fluorine than those from Pohorje marbles, however it does not contain chlorine, which is present in apatite from Pohorje.

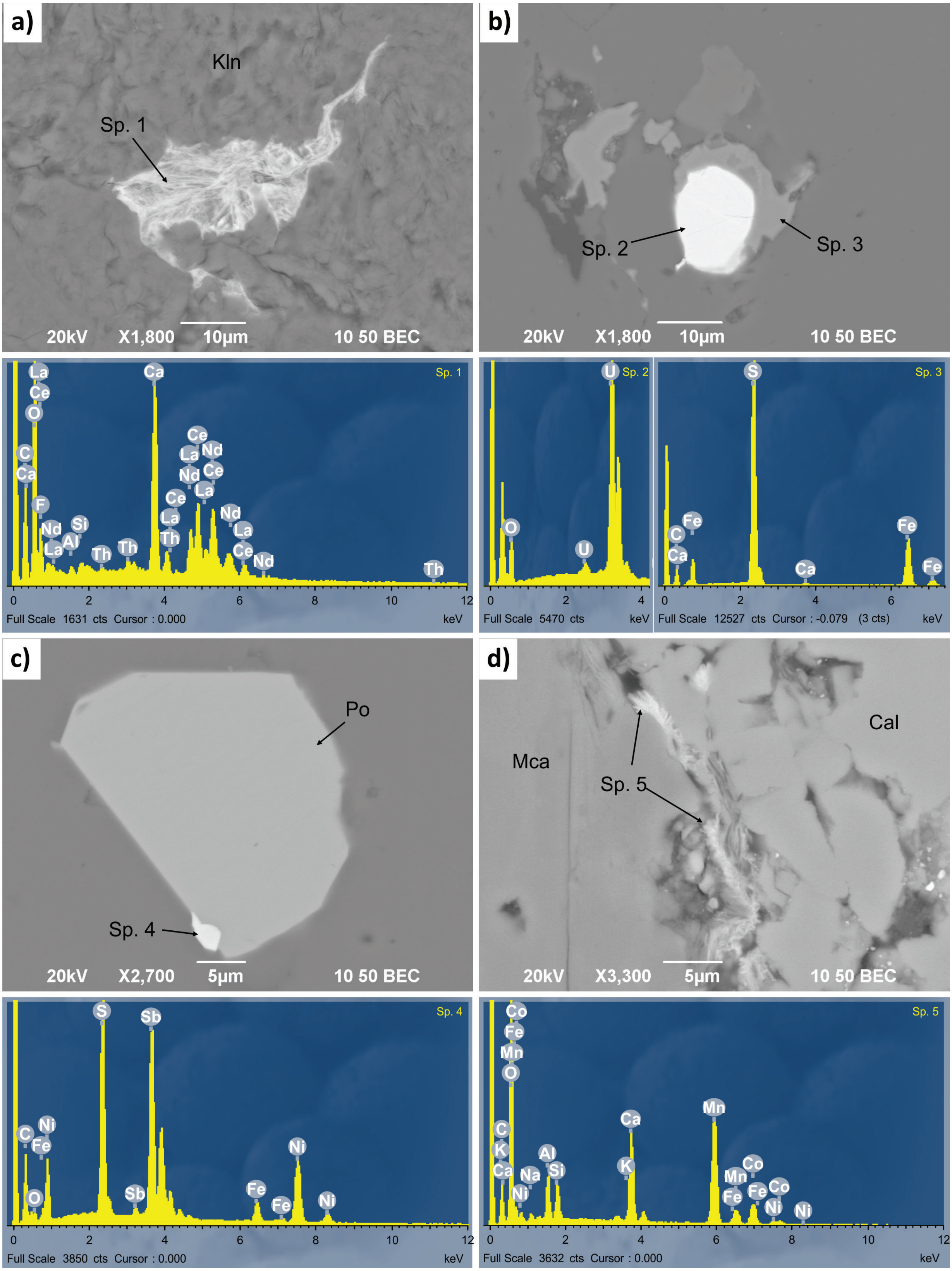

Fig. 3. SEM (BSE) images and EDS spectra of: a) grain of synchysite group mineral (Sp. 1), or pseudomorph of synchysite after petersenite in kaolinite (Kln) (marble from Košenjak); b) uraninite (Sp. 2) associated with pyrite (Sp. 3) (marble from Košenjak); c) ullmannite (Sp. 4) grain associated with pyrrhotite (Po) (marble from Košenjak) and d) asbolane (Sp. 5) aggregates at the contact between mica (Mca) and calcite (Cal) (marble from Strojna).

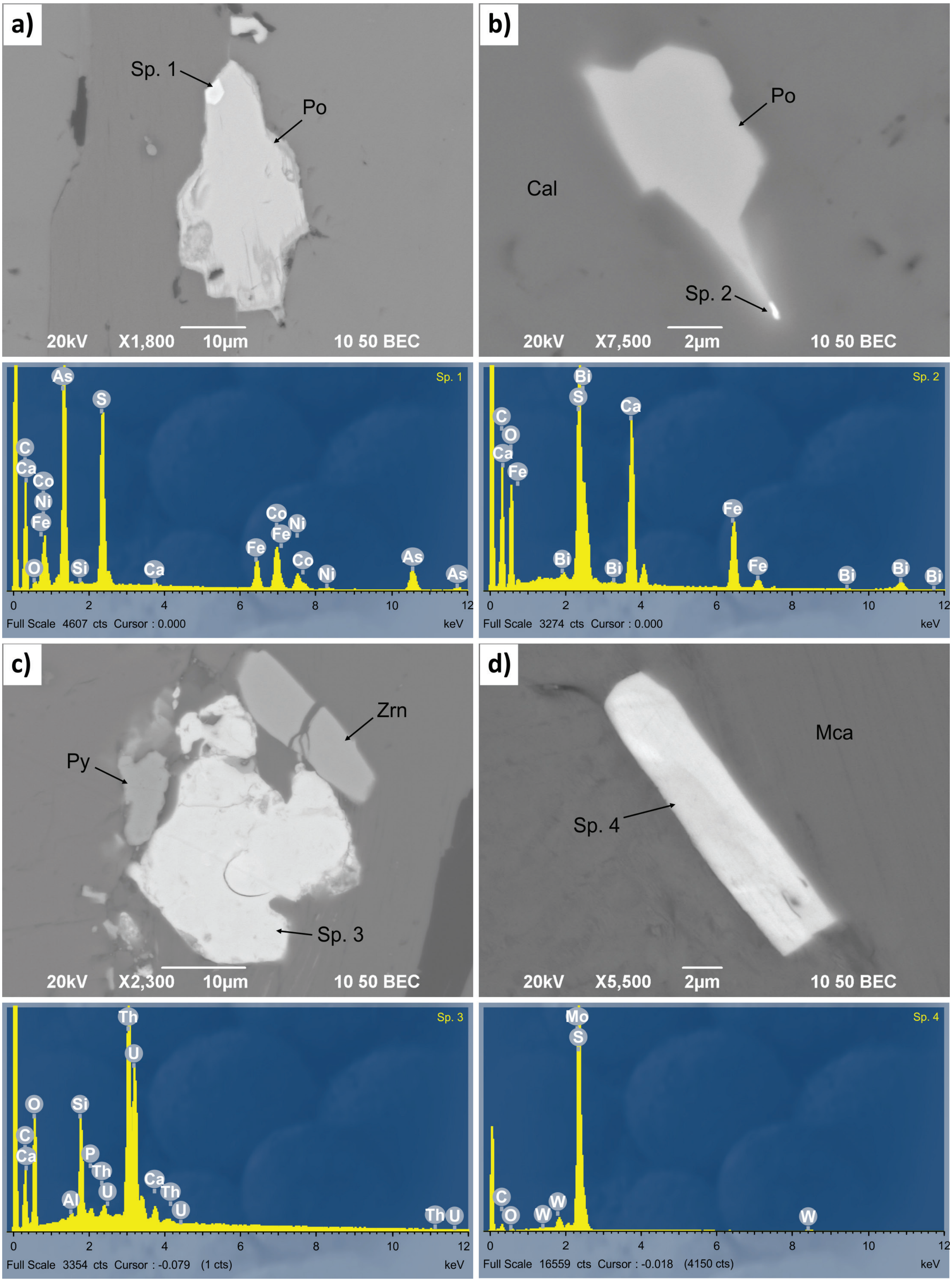

Fig. 4. SEM (BSE) images and EDS spectra of: a) inclusion of alloclasite or cobaltite (Sp. 1) in pyrrhotite (Po) (marble from Košenjak); b) inclusion of bismuth/bismuth oxide or carbonate (Sp. 2) in pyrrhotite (Po) at the boundary with calcite (Cal) (marble from Rimski kamnolom); c) thorite or huttonite (Sp. 3) associated with zircon (Zrn) and pyrite (Py) (marble from Košenjak) and d) molybdenite (Sp. 4) crystal enclosed in mica (Mca) (marble from Košenjak).

In all investigated marbles, 39 minerals or mineral groups were identified besides calcite and dolomite. For the first time in Slovenian marbles, minerals of synchysite group, or pseudomorphs of synchysite after petersenite, bastnäsite, tungsten-bearing ilmenorutile, ullmannite, asbolane, alloclasite or cobaltite, bismuth/bismuth oxides or carbonates, thorite or huttonite, uraninite and molybdenite were observed.

Although there are some differences in mineral assemblages between marbles from different locations, which are likely a consequence of different sedimentary environment and conditions and degree of metamorphism, they could also reflect heterogeneous nature of investigated marble sites and limited number of inspected samples. Based merely on mineral assemblages, we cannot argue to distinguish between marble localities of the three different massifs.

However, the differences in composition of very common minerals, such as calcite, titanite and apatite that are widespread in marbles from all three massifs, should enable rough distinction between more distant locations and marbles of different metamorphic grades, but not between individual sub-localities.

Established differences in mineral assemblages and chemical composition of common minerals could be useful for identification of sources of marbles.

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