

Minerals of Pohorje marbles

Minerali pohorskih marmorjev

Miha JERŠEK¹, Sabina KRAMAR², Simona SKOBE³, Nina ZUPANČIČ^{3,4} & Viljem PODGORŠEK⁵

¹Slovenian Museum of Natural History, Prešernova 20, SI-1000 Ljubljana

²Slovenian National Building and Civil Engineering Institute, Dimičeva ul.12, SI-1000 Ljubljana

³University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology, Aškerčeva 12, SI-1000 Ljubljana, Slovenia

⁴Ivan Rakovec Institute of Palaeontology, ZRC SAZU, Novi trg 2, SI-1000 Ljubljana, Slovenia

⁵Kraigherjeva ulica 17, SI-2250 Ptuj, Slovenia

Prejeto / Received 4. 4. 2013; Sprejeto / Accepted 17. 6. 2013

Key words: marble, Pohorje, accessory minerals, tremolite, vesuvianite, diopside

Ključne besede: marmor, Pohorje, akcesorni minerali, tremolit, vezuvianit, diopsid

Izvleček

Na Pohorju izdanzajo pretežno kalcitni marmorji, ki ponekod prehajajo v dolomitne. Karbonatne kamnine, iz katerih so nastali, so vsebovale tudi detritične minerale, ki so se med metamorfozo ohranili ali pa prešli v nove minerale. Raziskali smo minerale v marmorjih s Pohorja, ki so kot kristali vidni s prostim očesom ali z lupo 10 x povečave in s pomočjo binokularnega mikroskopa. Z ramansko mikrospektroskopijo, SEM-EDS analizo in na osnovi morfoloških značilnosti smo določili 17 različnih mineralov, med katerimi so, poleg kalcita, najpogostejši in obenem tudi najbolj značilni tremolit, diopsid, grosular in epidot. Prvič sta v pohorskih marmorjih opisana vezuvianit in scapolit. Ploskovno bogati so kristali kremenca, ki vsebujejo igličaste vključke amfibola. Drugi minerali, ki dopolnjujejo mineralno paragenozo marmorjev, so različni minerali sljud, minerali kloritove skupine, glinenci, magnetit, titanit, pirit in grafit. Določena mineralna združba nam razkriva mineralno pestrost pohorskih marmorjev in nam ponuja nove izzive za raziskovanje značilnosti in razmer pri nastanku te plemenite kamnine, ki so jo cenili in izkoriščali že Rimljani, danes pa ponovno dobiva svojo veljavo in prepoznavnost.

Abstract

In the Pohorje Mts, mostly outcrops of calcite marble can be found, which in places turn into dolomite marbles. The protolith carbonate rocks contained also detrital minerals, which remained unchanged or formed new minerals during metamorphism. Minerals in the Pohorje marbles that can be seen as crystals with the naked eye or 10x magnifying loupe and with binocular microscope were investigated. With the aid of Raman microspectroscopy, SEM-EDS analysis and on the basis of morphological characteristics, the presence of 17 different minerals or group of minerals was confirmed. The most numerous and also the most significant were, apart from calcite, tremolite, diopside, grossular and epidote. For the first time, vesuvianite and scapolite were described in the Pohorje Mts. Particularly rich, as far as crystal faces are concerned, were the crystals of quartz that contained needle-like amphiboles. Other minerals that well supplemented the mineral paragenesis were different minerals of mica and chlorite group, feldspars, magnetite, titanite, pyrite and graphite. The determined mineral association revealed the mineral diversity of Pohorje marbles, offering us a new challenge for the investigation of the characteristics and conditions during the origin of this noble rock, which was highly esteemed already by the Romans, while today it is regaining its value and recognisability.

Introduction

The thick Pohorje forests still hide many interesting mineral associations. This is also the case of Pohorje marbles. Thanks to various collectors, particularly Viljem Podgoršek and Franci Golob, who carried out extensive field sampling, we have been given an opportunity to analyse the macroscopically visible crystals in the marble. The Pohorje marbles, which were highly esteemed already by the Romans, have thus been supplemented by some new minerals, which may contribute to the characterization of this rock.

Metamorphism of relatively pure limestone and dolomite yields generally marble and dolomarmarble (BEST, 2007). Impure carbonate protoliths that contain variable amounts of quartz grains and shaly material may include, in addition to calcite, dolomite and quartz, as well as diopside, tremolite, talc, phlogopite, wollastonite, calcic plagioclase, vesuvianite, forsterite and grossular-andradite (BEST, 2007). Therefore, the presence of the minor content of non-carbonate minerals corresponds to the chemistry and mineralogy of the protolith and its metamorphic history. Mineral

assemblages, and therefore accessory minerals, provide crucial information on temperature and pressure during metamorphism, i.e. metamorphic facies (BEST, 2007). Some mineral species are particularly good traces since, alone, they may point to the provenance of the host marble (CAPEDRI et al., 2004; ORIGLIA et al., 2011; TAEELMAN et al., 2012). For example, fluorite points at Anatolian marbles, in particular to Marmara, Mugla/Salkim, or Balikesir/Kocoglu; zoisite to Naxos, and rare earth-containing epidote to Mugla/Golkuc; aspidolite is unique to Marmara, whereas margarite occurs at Marmara and Samos, and paragonite at Marmara, Aydin and Iraklia. Plogopite occurs at Marmara and Mugla/Salkim among the Anatolian marbles, and at Thasos, Naxos, Paros and Penteli among the Greek marbles; it may be worth noting that phlogopite is absent from Carrara marble (CAPEDRI et al., 2004). By contrast, plagioclase is typical of Carrara and Aydin among the white marbles, and of Mani and Mugla/Golkuc among the red coloured marbles (CAPEDRI et al., 2004).

On the other hand, some authors argue (LAZZARINI et al., 1980) that the accessory minerals themselves do not seem to have much diagnostic value owing to the wide distribution and frequent occurrences of common minerals like quartz, epidote and mica, and because of the absence of rare or special minerals. They may be used successfully in combination with other parameters for the characterisation of the marbles (CAPEDRI et al., 2004), e. g. geographical distribution as well as metamorphic history of the marble (BUCHER & FREY, 2002).

Within this study we focused only on determination of minerals, which are large enough to be seen macroscopically or with a 10x magnifying loupe.

Geological setting

The Pohorje Mts represent the south-eastern margin of the Eastern Alps. From the west to the south, Pohorje is bounded by the Labot fault and by the Periadriatic zone (MIOČ, 1978, 1983; MIOČ & ŽNIDARČIČ, 1977, 1983, 1989), whereas on the northern side the mid-Miocene Ribnica through separates Pohorje from the mountains of similar lithology and structure. On the eastern side, Pohorje gently dips below Plio-Quaternary sediments.

The Eastern Alps consist of a system of large nappes formed during the Eoalpine orogeny (FRANK, 1987; SCHMID et al., 2004, FODOR et al., 2008). Pohorje Mts are part of the Austroalpine nappe (PLACER, 2008). The deepest tectonic unit, the Pohorje nappe (JANAK et al., 2006), is mainly composed of medium- to high-grade (HP) metamorphic rocks – gneisses, mica schists and amphibolites with marble and quartzite. These rocks form a strongly foliated matrix along sporadic eclogite lenses and two main serpentinite bodies (HINTERLECHNER-RAVNIK, 1971, 1973; MIOČ, 1978). The evidence of ultra-high-pressure (UHP) metamorphism in eclogites was confirmed by JANAK et

al., 2004. The timing of HP/UHP metamorphism in the Pohorje nappe is Cretaceous (THÖNI, 2002; MILLER et al., 2005; CORNELL et al., 2007) and Tertiary – Early to Middle Miocene (FODOR et al., 2002). The Pohorje nappe is overlain by a nappe of weakly metamorphosed Paleozoic rocks, mainly low-grade metamorphic slates and phyllites (HINTERLECHNER-RAVNIK, 1971, 1973; VRABEC, 2010). The upper nappe is built up of Permo-Triassic clastic sedimentary rocks, prevailing sandstones and conglomerates (HINTERLECHNER-RAVNIK, 1971, 1973; VRABEC, 2010). The entire nappe stack is overlain by early Miocene sediments, which belongs to the syn-rift basin fill of the Pannonian Basin (FODOR et al., 2003).

Also, a large granodiorite body with a smaller dacite part in its north-western section (DOLAR MANTUANI, 1935; FANINGER, 1970; ZUPANČIČ, 1994a, b) is intruded into the central part of the massif. It is of the Miocene age (18–19 Ma; TRAJANOVA et al., 2008; FODOR et al., 2008). The boundary of the pluton is locally tectonized, but the original magmatic contact is marked by a thin contact aureole (MIOČ & ŽNIDARČIČ, 1977; ŽNIDARČIČ & MIOČ, 1988; MIOČ & ŽNIDARČIČ, 1989). In the contact with muscovite micashist, the contact aureole is missing as the rocks have already been crystallised in almandine amphibolites facies (HINTERLECHNER-RAVNIK, 1973).

GERMOVŠEK (1954) distinguished three genetic marble types. The major type present in SE Pohorje was described as dynamometamorphic marbles and associated them with micashists. In the northern part of Pohorje, there are small outcrops of metamorphosed Upper Cretaceous limestones, while in the NW part of Pohorje marbles in contact with dacite are present. According to HINTERLECHNER-RAVNIK & MOINE (1977), the marble level occurs in two separated areas in the southern and eastern parts of the massif, clearly exposed between the Oplotniščica and Dravinja brooks, and north of Šmartno, towards Ruše. Here, marbles occur between biotite ± muscovite schists and gneiss and flaser gneiss with ± almandine ± kyanite and amphibolite varieties (HINTERLECHNER-RAVNIK & MOINE, 1977). Marble is more abundant in the southern part of the massif, where it represents up to 30% of the horizon, than in its northern part (HINTERLECHNER-RAVNIK & MOINE, 1977; JARC & ZUPANČIČ, 2009). The marble is coarse grained, rarely fine grained; in contacts with phyllite schists it is poorly crystallized and brecciated (HINTERLECHNER-RAVNIK, 1971). The marble is white, or coloured due to accessory minerals, such as graphite and pyrite (grey colour) or silicate minerals, such as amphiboles and biotite (greenish and brownish to violet coloured). The dolomite marble is also present (HINTERLECHNER-RAVNIK, 1971).

The textures of marbles are granoblastic, sutured and blastomillonic. Calcite crystals exhibit twin lamellae, rhombohedral cleavage and undulatory extinction, which indicates the growth under pressure (HINTERLECHNER-RAVNIK, 1971). The accessory minerals are quartz, Na-rich plagi-

clase, tremolite, green hornblende, diopside, forsterite, mica (muscovite and biotite group), rarely garnets, graphite, pyrite, and the products of retrograde metamorphism: chlorite, epidote, clinzoisite, serpentine over forsterite and limonite (HINTERLECHNER-RAVNIK, 1971; JARC & ZUPANČIČ, 2009). From the vicinity of Zreče, GERMOVŠEK (1954) reported on wollastonite rich marble with transition to wollastonite-bearing rock.

Materials and methods

Marble samples from different Pohorje quarries were collected by Viljem Podgoršek and Franc Golob, who registered several mineral sites in the period between August 12th 2011 and July 24th 2012. We have selected, examined and analysed 16 marble samples from the area of Bojtina quarry, three from the Skomarje quarry, two from the marble quarry at Gorenja vas near Zreče, two from Planica, and one from Frajhajm near Pregel and Čadram.

Raman spectroscopy has been used successfully in nearly all geoscience disciplines and virtually all kinds of samples have been studied using this technique (NASDALA et al., 2004). Raman spectroscopy is a technique based on inelastic scattering of monochromatic light - sample is illuminated with a laser beam. Scattered light results in Raman spectrum that is characteristic of a certain mineral. Raman microspectroscopy does not require special preparation of samples for analyses, but enables us to identify minerals even non-destructively. Furthermore, tiny crystals that due to the impossibility of separation or preparation of such diminutive amounts could not be analysed by other techniques, such as X-ray diffraction analysis, could be identified. Raman spectra of samples were obtained with a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer equipped with an Olympus BXFM optical microscope. Measurements were made using a 785 nm laser excitation line, and the Leica 50 \times objective was used. The spectral resolution was about 1 cm⁻¹.

The morphology and chemical compositions of the selected samples were additionally examined using Scanning Electron Microscopy (SEM) JEOL 5500 LV SEM equipped with the Energy Dispersive X-Ray spectrometry (EDS), at accelerating voltage 20 kV and working distance 20 mm. Prior to the analyses, samples were carbon coated. X-ray spectra were optimized for quantification using cobalt optimization standard, and the correction of EDS data was performed on basis of the standard ZAF-correction procedure included in the INCA Energy software.

Results and discussion

The identified minerals in marble with their localities are given in Table 1. All of the collected samples have more or less fully developed crystals of different minerals, which could have been established already with the naked eye, a 10 \times mag-

nifying loupe, or with the aid of a binocular microscope.

A total of 17 different minerals were identified in marbles from the Pohorje Mts. The largest crystals are secondary calcite crystals of younger generation that occur in nests of calcite marbles. The most abundant and also the larger crystals found are pyroxene diopside and amphibole tremolite. Significant minerals are grossular, scapolite, epidote and vesuvianite. Among micas, quite frequently group of minerals, biotite and muscovite were identified. Also, some minerals of chlorite group were detected. Quartz (sometimes with inclusions of amphibole), magnetite, titanite and pyrite that is sometimes limonitised are less abundant among minerals easily seen with the naked eye. We also identified some feldspars; plagioclase and orthoclase. Small inclusions in calcite are identified as graphite.

Hereinafter, macroscopic characteristics of selected minerals will be given.

Calcite

Calcite crystals in nests of marbles are white, colourless and slightly yellow coloured. Dominant crystal face is a step rhombohedron, modified by other rhombohedrons (Figs. 1 and 2). Calcite crystals are up to 1 cm high. Calcite crystals with step rhombohedrons are characteristic of the final stage of crystallisation in metamorphic rocks, referred to as a continuous drop of temperature or a successive change in the solutions' pH (KOSTOV & KOSTOV, 1999).



Fig. 1. Corroded calcite crystals in a rare nest in marbles from Bojtina, 10 \times 6 cm. Franc Golob's Collection

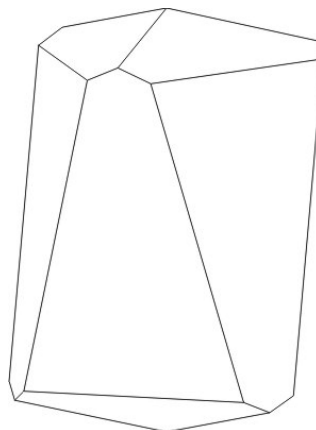


Fig. 2. Crystals of calcite from Bojtina marble have developed step rhombohedron faces (\approx 071) and rhombohedron (021).

Diopside

Apart from calcite, diopside is very common mineral found in the Pohorje marbles (Figs. 3 and 4). It is usually green, olive green to dark green or even colourless (Fig. 3). For the most part, the crystals are seemingly opaque, and it is only rare smaller samples that are transparent. Exceptions are the utterly colourless and transparent diopside crystals from Frajhajm near Pregel. Here and there, diopside is finely granulated and massive. Individual olive green crystals with glassy shine are more than 20 mm long. The largest diopside crystal is dark green and 50 mm high. On the parts, where crystal planes have been preserved, the crystal has silky lustre.



Fig. 3. 10 mm high crystals of dark green diopside in the Bojtina marble. Viljem Podgoršek's Collection

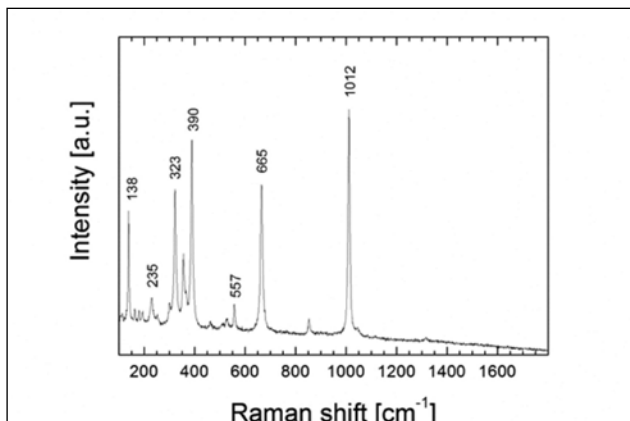


Fig. 4. Raman spectrum of diopside from Bojtina marble

Tremolite

Tremolite (Fig. 5) occurs in prismatic elongated crystals. They are colourless to white and form up



Fig. 6. Radial clusters of tremolite from Bojtina marble, 10 x 6 cm. Viljem Podgoršek's Collection

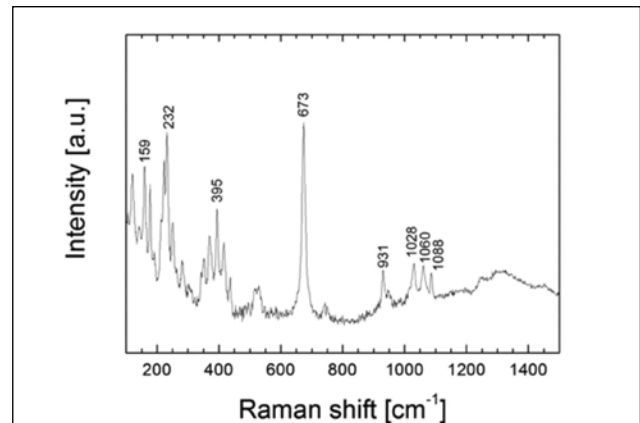


Fig. 5. Raman spectrum of tremolite from Skomarje marble

to 25 mm long crystals. They can develop as separate crystals or form radial clusters with a diameter of up to 40 mm (Fig. 6).

Grossular

The honey-brown crystals of garnet mineral grossular (Fig. 7) occur in marble alongside to epidote, biotite and pyrite. Grossular is partially massive and without apparently developed crystal surfaces, or in separate crystals that do not exceed 1 mm in size (Fig. 8). On separate crystals, surfaces of rhombic dodecahedron can be determined (Fig. 9). The tiny crystals are transparent with high lustre.

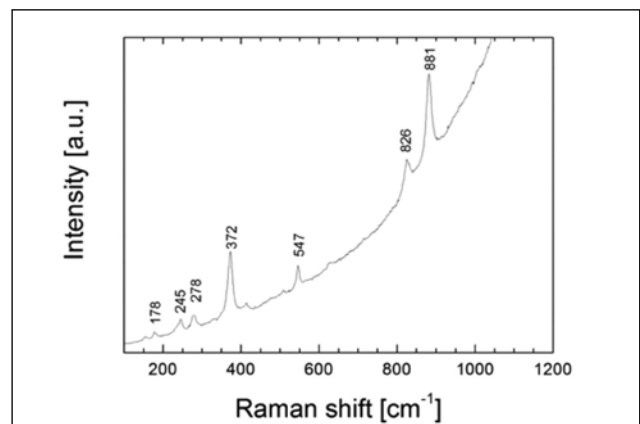


Fig. 7. Raman spectrum of grossular from Bojtina marble



Fig. 8. Honey-brown crystals of grossular from Bojtina marble measure up to 1 mm in diameter. Viljem Podgoršek's Collection

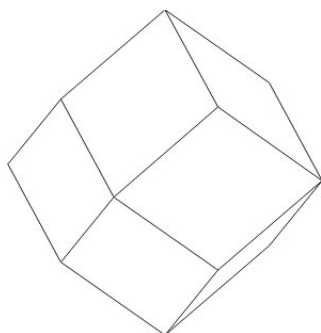


Fig. 9. The grossular in Bojtina marble has well-developed rhombic dodecahedron crystal faces (101).

Epidote

Epidote (Fig. 10) occurs in characteristic green, or less frequently in green-brownish crystals up to 15 mm in size. They are mostly translucent, less often transparent. The epidote crystals are explicitly prismatic, some have etched figures on crystal faces (Fig. 11).

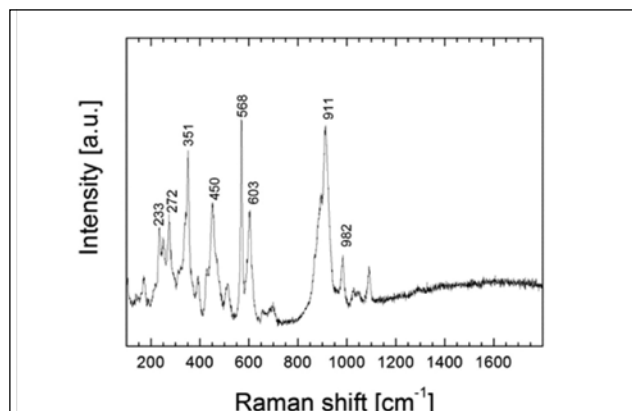


Fig. 10. Raman spectrum of epidote from Bojtina marble



Fig. 11. Epidote crystals in the Bojtina marble, 2.0 x 0.5 mm. Viljem Podgoršek's Collection

Vesuvianite

Vesuvianite crystals occur in hatches between calcite crystals. They are translucent to transparent and brown. The tiny up to a few mm long crystals are well-developed with crystal faces, where glassy lustre can be well seen. The crystals are medium to long prismatic (Figs 12 and 13) and have well-developed crystal faces of tetragonal prism of first and second order (110) and second order (100), tetragonal pyramid of second order (1.0.14.), and basal pinacoid (001).

According to the crystallogenic trend of vesuvianite (Kostov & Kostov, 1999), the vesuvianite prismatic crystals from Pohorje marbles indicate that they crystallised under lower temperature.



Fig. 12. The prismatic vesuvianite crystal (height of the crystal is 3 mm) in a hatch with calcite crystals in the Bojtina marble. Viljem Podgoršek's Collection



Fig. 13. Long prismatic crystal of vesuvianite from Bojtina with well-developed crystal faces of tetragonal prism of first and second order, tetragonal bipyramid of second order, and basal pinacoid.

Magnetite

Magnetite occurs in tiny up to 2 mm large crystals, together with colourless calcite crystals, sometimes as inclusions in them. They are opaque, grey and almost black with almost metallic lustre (Fig. 14). Some individual crystals have attractively developed octahedron crystal faces (Fig. 15), while the great majority of crystals are granular and of fairly irregular shapes.



Fig. 14. Tiny up to 1 mm large magnetite crystals rarely occur in crystals with well-developed crystal faces from Bojtina marble. Viljem Podgoršek's Collection

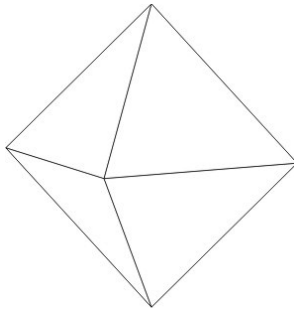


Fig. 15. Individual magnetite crystals from Bojtina have well-developed crystal faces of an octahedron (111).

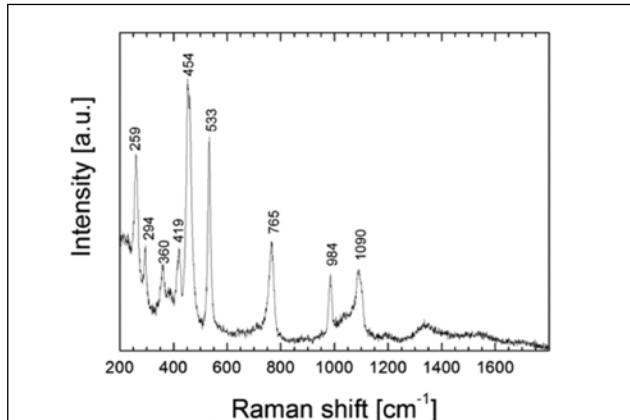


Fig. 16. Raman spectrum of scapolite from Bojtina marble



Fig. 17. Scapolite in the Bojtina marble is in white opaque crystals, the length of which does not exceed 25 mm. Viljem Podgoršek's Collection

Scapolite

Scapolite (Fig. 16) is a group of solid solution minerals with end members meionite $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$ and marialite $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$. In Pohorje marbles, scapolite occurs in white transparent, seemingly opaque crystals up to 30 mm in size (Fig. 17). The crystals are relatively rare, cracked and distinctly prismatic.

Quartz

Quartz is massive and white in the form of few tens of cm lenses in a marble. Rarely, crystals of quartz are developed in well formed colourless crystals (Fig. 18). They are mostly up to 1 cm high. The largest crystal discovered is 2 cm in length. Crystal morphology of quartz exhibits also left Douchinné twin. Crystals are twinned as left Douchinné twin. Crystals have sometimes inclusions of tiny needle-like inclusions of amphibole (Fig. 20).



Fig. 18. Quartz crystal (15 mm high) with inclusion of a needle-like amphibole from Bojtina marble. Franc Golob's Collection

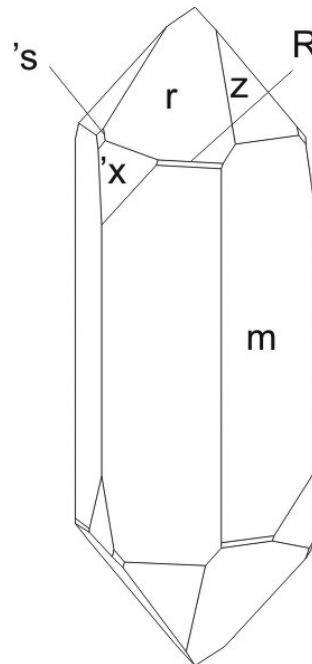


Fig. 19. Quartz crystals from Bojtina have well developed crystal faces of hexagonal prism of 1st order **m** (100), rhombohedron of 1st order **r** (101), negative rhombohedron of 1st order **z** (011), step rhombohedron **R** ($\approx 20.0.1.$), trigonal bipyramid of 2nd order **'s** (-121) and trapezohedron **z** (-561).

Pyrite

Pyrite occurs in limonitised crystals up to 5 mm in size. Smaller crystals, up to 1 mm, have well-developed crystal forms of cube and octahedron (Fig. 20). Such crystals can be found among quartz crystals (Fig. 21).



Fig. 20. Limonitised pyrite crystal among two quartz crystals with inclusion of a needle-like amphibole from Bojtina marble (5 x 4 mm). Franc Golob's Collection

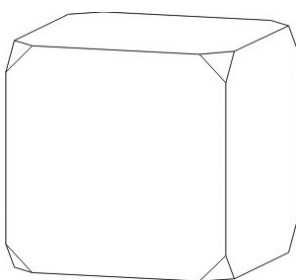


Fig. 21. Pyrite crystal with crystal faces of cube and octahedron. (Bojtina)

Other minerals

In Pohorje marbles, some other minerals were identified as well. Thus, flakes of mica can also be found, which are brownish and totally transparent (biotite group) or colourless and transparent, too (muscovite). Crystals of chlorite group minerals are green and up to 1 mm in size (Fig. 22). Titanite



Fig. 22. Bojtina minerals from chlorite group are overgrown with calcite rhombohedrons. Viljem Podgoršek's Collection



Fig. 23. Bojtina titanite crystal with crystal forms [001] and [111], 2 mm. Franc Golob's Collection.

is a yellow-coloured and wedge-shaped crystal up to 3 mm in size (Fig. 23). Amongst feldspars, plagioclases and orthoclase were determined. Graphite crystals are found only in two samples; one from Čadram and the second from Bojtina.

Based on the morphological features, Raman microspectroscopy and SEM/EDS analyses (Tab. 2), it was possible to confirm the presence of 17 different minerals or group of minerals, i.e. calcite, quartz, tremolite, grossular, vesuvianite, epidote, diopside, scapolite group, micas (muscovite and biotite group), feldspars (orthoclase and plagioclase), titanite, chlorite group, magnetite, pyrite and graphite. For the first time, vesuvianite and scapolite were observed in Pohorje Mts., whereas other minerals have already been determined also

Table 1. Identified minerals of marbles with their localities and analytical method used Legend: □ Raman microspectroscopy; ● SEM/EDS; ◇ morphology

MINERAL/ LOCALITY	Bojtina	Skomarje	Gorenja vas	Planica	Frajhajm	Čadram
Calcite	◇	◇	◇	◇□	◇	
Tremolite	◇□	□●	◇□	□		
Grossular	◇□●					
Vesuvianite	◇□●					
Epidote	◇□●				□◇	
Diopside	◇□●	◇			□●	
Scapolite	◇□●					
Magnetite	◇□					
Quartz	◇					
Biotite	◇	◇	◇			
Muscovite	◇□					
Clinochlor	◇□●	●	□			
Titanite	◇□					
Pyrite	◇	◇	◇●			
Orthoclase	□					
Plagioclase	□					
Graphite	□					□

by microscopical investigations (e.g. HINTERLECHNER-RAVNIK, 1971, 1973; Mioč, 1978, 1983; JARC & ZUPANČIČ, 2009). Both vesuvianite and scapolite are common minerals in metamorphic rocks.

All of the identified minerals could be found in marbles (BUCHER & FREY, 2002; BEST, 2007; INTERNET). Sedimentary carbonate rocks consist predominantly of carbonate minerals, but the rocks often contain variable amounts of quartz (BUCHER & FREY, 2002). During metamorphism of these rocks, chemical reactions in the CaO – MgO – SiO₂ system are thus very common indeed and, besides calcite, dolomite and quartz, the formation of non-carbonate minerals such as talc, tremolite, diopside, forsterite, antigorite, periclase, brucite and wollastonite (BUCHER & FREY, 2002) occur. Depending on the P-T conditions of metamorphism, the mineral assemblages of the above-mentioned minerals are stable and, in fact, the presence or absence of some mineral defines the conditions. The carbonate protolith usually contains some shaly material (BEST, 2007), which is also the source for Fe, Mg and other components. Thus, the final mineral composition is mainly dependent of the chemistry of the source material. In Pohorje marbles, beside carbonates and quartz, tremolite and diopside are very common minerals. These mineral assemblages are typical in regional metamorphism of limestones and dolomites and also in contact metamorphism of the carbonates (BUCHER & FREY, 2002). Also, other present minerals, such as garnets, vesuvianite and scapolite, could be the products of regional or contact metamorphism (INTERNET). Given that the minerals have been determined only by morphological feature, Raman microspectroscopy and SEM/EDS, the type of metamorphism could not be established.

Minerals, such as epidote, clinoclhor, are typical products of retrograde metamorphism, which has been already established in Pohorje metamorphic rocks (HINTERLECHNER-RAVNIK, 1971).

Therefore, numerous present non-carbonate minerals of Pohorje marbles are the result of the very complex polimetamorphic history of the Pohorje rocks with a combination of progressive and retrograde metamorphisms as interpreted by HINTERLECHNER-RAVNIK (1971, 1973).

Table 2. Average (of two measurements) elementary compositions (wt%) of selected mineral samples from Bojtina marble, determined with EDS

O	Na	Mg	Al	Si	Cl	Ca	Fe	K	Mineral
70,83	-	2,46	6,34	15,63	1,50	1,68	1,55	-	clinoclhor
63,81	-	11,01	-	20,71	-	4,47	-	-	tremolite
61,39	-	-	11,55	14,49	-	9,94	2,62	-	epidote
66,84	-	6,50	1,24	17,34	-	7,32	1,37	-	diopside
73,79	-	0,82	5,75	10,84	-	8,21	0,59	-	vesuvianite
66,90	1,88	0,73	10,33	16,40	-	4,14	-	1,69	scapolite
64,25	-	-	7,87	14,03	-	11,98	1,86	-	grossular

Conclusions

The marbles from Pohorje Mts contain numerous minerals, which could be easily seen by the naked eye. They are not very common and sometimes it is hard to see them owing to their rarity and size. Nevertheless, we managed to find, collect and study them.

Morphological features of the minerals from 25 samples were determined by 10x magnifying loupe and binocular microscope. Besides carbonate minerals (calcite), numerous silicate minerals, oxides and sulphides with graphite have been observed. A total of 17 minerals or mineral groups were identified based on the morphology observation, Raman microspectroscopy and SEM/EDS analyses. Thus the presence of calcite, quartz, tremolite, grossular, vesuvianite, epidote, diopside, scapolite group, micas (muscovite and biotite group), feldspars (potassium feldspar and plagioclase), titanite and chlorite group among silicate minerals, and magnetite, pyrite and graphite was confirmed. The calcite crystals are up to 1 cm long, quartz crystals up to 2 cm and tremolite crystals are up to 25 mm long and could form radial clusters with a diameter of up to 40 mm and epidote crystals are up to 15 mm. The biggest found minerals with clear morphological features belong to diopside (50 mm) and scapolite group. Although scapolite crystals are relatively rare, they are up to 30 mm long. The sizes of the other accessory minerals do not exceed few mm. Quartz crystals with many well developed crystal faces and inclusions of a needle-like amphibole have also been found. For the first time, vesuvianite and scapolite were observed in Pohorje Mts.

The mineral assemblages are not significant for the specific locality. Therefore, the examined mineral sites could not have been distinguished only by the presence or absence of the specified minerals.

The mineral assemblage of Pohorje marble is typical of the marble metamorphosed from carbonate rich protolith (calcite was prevailing), but with variable amounts of quartz and other shaly materials. The Pohorje marbles are predominantly calcitic, with some dolomite present as well as with some silicate minerals such as quartz, tremolite, diopside, which are typical mineral assemblages for regional metamorphosis of limestones and dolomites, and also for contact metamorphosis of carbonate rocks (BUCHER & FREY, 2002). Therefore, the type and grade of metamorphosis could not have been determined from minerals determined by morphological investigations, Raman microspectroscopy and SEM/EDS analyses. The determined mineral assemblage from Pohorje marbles clearly indicates a very complex history of this area.

References

- BEST, M. G. 2007: Igneous and metamorphic petrology. Second Edition, Blackwell Publishing: 729 p.
- BUCHER, K. & FREY, M. 2002: Petrogenesis of metamorphic rocks. Seventh Edition, Springer, Berlin: 341 p.
- CAPEDRI, S., VENTURELLI, G. & PHOTIADES, A. 2004: Accessory minerals and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of marbles from the Mediterranean area. *Journal of Cultural Heritage*, 5/1: 27–47, doi:10.1016/j.culher.2003.03.003.
- CORNELL, D., JANÁK, M., FROITZHEIM, N., BROSKA, I., VRABEC, M. & DE HOOG, J.C.M. 2007: Ion microprobe U-Pb zircon dating of gneiss from the Pohorje, Eastern Alps and implications for deep subduction of a coherent continental crust. In Abstract volume, 8th Workshop on Alpine Geological Studies, Davos, 10–12 October 2007: 15–16.
- DOLAR MANTUANI, L. 1935: Tonalite and aplite ratio of Pohorje massiv. *Geološki Anali Balkanskog Poluostrva*, 12: 1–165.
- FANINGER, E. 1970: The tonalite of Pohorje and its differentiates. *Geologija*, 13: 35–104.
- FODOR, L., JELEN, B., MÁRTON, E., ZUPANČIČ, N., TRAJANOVA, M., RIFELJ, H., PÉCSKAY, Z., BALOGH, K., KOROKNAI, B., DUNKL, I., HORVÁTH, P., HORVAT, A., VRABEC, M., KRALJIČ, M. & KEVRIČ, R. 2002: Connection of Neogene basin formation, magmatism and cooling of metamorphics in NE Slovenia. *Geologica Carpathica*, 53 (special issue): 199–201.
- FODOR, L., BALOGH, K., DUNKL, I., PÉCSKAY, Z., KOROKNAI, B., TRAJANOVA, M., VRABEC, M., VRABEC, M., HORVÁTH, P., JANÁK, M., LUPTÁK, B., FRISCH, W., JELEN, B. & RIFELJ, H. 2003: Structural evolution and exhumation of the Pohorje-Kozjak Mts., Slovenia. *Annales Universitatis Scientiarum Budapestinensis, Sectio Geologica*, 35: 118–119.
- FODOR, L., GERDES, A., DUNKL, I., KOROKNAI, B., PÉCSKAY, Z., TRAJANOVA, M., HORVÁTH, P., VRABEC, M., JELEN, B., BALOGH, K. & FRISCH, W. 2008: Miocene emplacement and rapid cooling of the Pohorje pluton at the Alpine-Pannonian-Dinaric junction, Slovenia. *Swiss Journal of Geoscience*, 101/1: 255–271, doi 10.1007/s00015-008-1286-9.
- FRANK, W. 1987: Evolution of the Austroalpine elements in the Cretaceous. In: FLÜGEL, H.W. & FAUPEL, P. (eds.): *Geodynamics of the Eastern Alps*. Vienna: Deuticke: 379–406.
- GERMOVŠEK, C. 1954: Petrographic research of Pohorje in 1952. *Geologija*, 2: 191–210.
- HINTERLECHNER-RAVNIK, A. 1971: Metamorphic rocks of Pohorje mountains. *Geologija*, 14: 187–226.
- HINTERLECHNER-RAVNIK, A. 1973: Metamorphic rocks of the Pohorje mountains II. *Geologija*, 16: 245–269.
- HINTERLECHNER-RAVNIK, A. & MOINE, B. 1977: Geochemical characteristics of the metamorphic rocks of the Pohorje Mountains. *Geologija*, 20: 107–140.
- JANÁK, M., FROITZHEIM, N., VRABEC, M. & KROGH RAVNA, E.J. 2004: First evidence for ultrahigh-pressure metamorphism of eclogites in Pohorje, Slovenia: Tracing deep continental subduction in the Eastern Alps. *Tectonics*, 23/5, doi:10.1029/2004TC001641.
- JANÁK, M., FROITZHEIM, N., VRABEC, M., KROGH RAVNA, E.J. & DE HOOG, J.C.M. 2006: Ultrahigh-pressure metamorphism and exhumation of garnet peridotite in Pohorje, Eastern Alps. *J. metamorphic Geol.*, 24: 19–31, doi:10.1111/j.1525-1314.2005.00619.x.
- JARC, S. & ZUPANČIČ, N. 2009: A cathodoluminescence and petrographical study of marbles from the Pohorje area in Slovenia. *Chem. Erde*, 69: 75–80, doi:10.1016/j.chemer.2008.01.001.
- LAZZARINI, L., MOSCHINI, G. & STIEVANO, B. M. 1980: A contribution to identification of Italian, Greek and Anatolian marbles through a petrological study and the evaluation of Ca/Sr ratio. *Archaeometry*, 22/2:173–183.
- KOSTOV, I. & KOSTOV, R.I. 1999: *Crystak habits of mineral*, Prof. Marin Drinov Academic Publishing House & Pensoft Publishers, Sofia: 415 p.
- MILLER, C., MUNDIL, R., THÖNI, M. & KONZETT, J. 2005: Refining the timing of eclogite metamorphism: a geochemical, petrological, Sm-Nd and U-Pb case study from the Pohorje Mountains, Slovenia (Eastern Alps). *Contrib. Mineral. Petrol.*, 150: 70–84, doi:10.1007/s00410-005-0004-0.
- MIOČ, P. 1978: Osnovna geološka karta SFRJ 1:100,000. Tolmač za list Slovenj Gradec (L 33–55). Zvezni geološki zavod, Beograd: 74 p (in Slovenian with English summary).
- MIOČ, P. 1983: Osnovna geološka karta SFRJ 1:100,000. Tolmač za list Ravne na Koroškem (L 33–54). Zvezni geološki zavod, Beograd: 69 p.
- MIOČ, P. & ŽNIDARČIČ, M. 1977: Osnovna geološka karta SFRJ 1:100,000, list Slovenj Gradec (L 33–55). Zvezni geološki zavod, Beograd (in Slovenian).
- MIOČ, P. & ŽNIDARČIČ, M. 1983: Geološka karta 1:25.000, Vitanje, Vuzenica, Slovenska Bistrica, Ribnica na Pohorju, Oplotnica, Mislinja, Slovenj Gradec. Manuscript maps. Archive of the Geological Survey of Slovenia, Ljubljana (in Slovenian).
- MIOČ, P. & ŽNIDARČIČ, M. 1989: Osnovna geološka karta SFRJ 1:100,000. Tolmač za list Maribor in Leibnitz. Zvezni geološki zavod, Beograd: 60 p.
- NASDALA, L., SMITH, D.C., KAINDL, R. & ZIEMANN, M.A. 2004: Raman spectroscopy: Analytical perspectives in mineralogical research. In: BERAN, A. & LIBOWITZKY, E. (eds.): *Spectroscopic Methods in Mineralogy*, EMU Notes in Mineralogy, 6/7: 281–343.
- ORIGLIA, F., GLIOZZO, E., MECCHERI, M., SPANGENBERG, J.E., MEMMI, I.T. & PAPI, E. 2011: Mineralogical, petrographic and geochemical characterization of White and Coloured Iberian marbles in the context of the provenancing of some artefacts from Thamusia (Kenitra, Morocco). *European Journal for Mineralogy*, 23: 857–69.
- PLACER, L. 2008: Principles of the tectonic subdivision of Slovenia. *Geologija*, 51/2: 205–217, doi:10.5474/geologija.2008.021.

- SCHMID, S.M., FÜGENSCHUH, E., KISSLING, E. & SCHUSTER, R. 2004: Tectonic map and overall architecture of the Alpine orogen. *Eclogae Geol. Helv.*, 97/1: 93–117, doi 10.1007/S00015-004-1113-X.
- TAEELMAN, D., ELBURG, M., SMET, I., DE PAEPE, P., VANHAECKE, F. & VERMEULEN, F. 2012: White, veined marble from Roman Ammaia (Portugal): Provenance and use, *Archaeometry*, 55/3: 370–390, doi: 10.1111/j.1475-4754.2012.00691.x
- THÖNI, M. 2002: Sm-Nd isotope systematics in garnet from different lithologies (Eastern Alps): age results, and an evaluation of potential problems for garnet Sm-Nd chronometry. *Chem. Geol.*, 185/3-4: 255–281, doi:10.1016/S0009-2541(01)00410-7.
- TRAJANOVA, M., PÉCSKAY, Z. & ITAYA, T. 2008: K-Ar geochronology and petrography of the Miocene Pohorje Mountains batholith (Slovenia). *Geologica Carpathica*, 59: 247–260
- VRABEC, M. 2010: Garnet peridotites from Pohorje: petrography, geothermobarometry and metamorphic evolution. *Geologija*, 53/1: 21–36, doi:10.5474/geologija.2010.002.
- ZUPANČIČ, N. 1994a: Petrographical characteristics and classification of magmatic rocks of Pohorje. *Rudarsko-metalurški zbornik*, 41: 101–112
- ZUPANČIČ, N. 1994b: Geochemical characteristics and origin of magmatic rocks of Pohorje. *Rudarsko-metalurški zbornik*, 41: 113–128.
- ŽNIDARČIČ, M. & Mioč, P. 1988: Osnovna geološka karta SFRJ 1:100,000, list Maribor in Leibnitz (L 33–56, L 33–44). Zvezni geološki zavod, Beograd).
- INTERNET: <http://www.mindat.org/> (28.3.2013)