Int J Earth Sci (Geol Rundsch) (2009) 98:357–366
DOI 10.1007/s00531-007-0244-5

REVIEW ARTICLE

Decorative marbles from the Krkonoše-Jizera Terrane (Bohemian Massif, Czech Republic): provenance criteria

Aneta Šťastná · **Richard Přikryl**

Received: 11 September 2006 / Accepted: 19 August 2007 / Published online: 26 September 2007

Abstract Marbles from western part of the Krkonoše-Jizera Terrane (northern part of the Bohemian Massif) have been studied to obtain mineropetrographic and chemical reference data for provenance studies. Samples from six different quarries were analysed by mineralogical-petrographic and geochemical methods (optical microscopy, X-ray diffraction, stable isotope ratio analysis, cathodoluminescence, bulk magnetic susceptibility). Petrographic characteristics permit a distinction between fine-grained to medium-grained marbles from the Jizera Mts (amphibolite metamorphic facies) and fine-grained marbles from the Ještěd Mts (low-grade greenschist facies). The samples studied are mainly calcitic, with the exception of those from Raspenava in which dolomite is abundant in two types. The mineralogical composition of the insoluble residues is clinochlore ± serpentine ± tremolite ± diopside ± pyrite + magnetite in case of the locality Raspenava and clinochlore + muscovite ± quartz ± pyrite ± rutile ± haematite in case of the localities from the Ještěd Mts. δ^{13}C and δ^{18}O variations in primary and secondary carbonate phases allow to distinguish genetically different carbonate veins and permit quarry separation in one case (Raspenava, Jizera Mts). The δ^{13}C and δ^{18}O values of the groundmass range from –1 to +3‰ and from –8 to –20‰ (PDB), respectively. The δ^{13}C and δ^{18}O values of secondary carbonate veins decrease to –3‰ and reach more negative values up to –26‰ in case of δ^{18}O. The fabric of cathodomicrofacies allows the distinction between calcite and dolomite, except three localities (Pilínkov, Horní Hanychov, Jitrava—rose type) with majority of quenchers (high content of iron in carbonate). The genetically different calcite is characterised by a pale and dark orange luminescence distribution. Serpentine, tremolite, forsterite, opaque minerals and quartz have no luminescence and very dull luminescence, respectively. The majority of studied marbles exhibits low values of the bulk magnetic susceptibility, with the exception of those from Raspenava rich in magnetite.

Keywords Krkonoše-Jizera Terrane · Marbles · Provenance study · Isotopes

A. Šťastná (✉) · R. Přikryl
Faculty of Science, Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University in Prague, Albertov 6, 128 43 Praha 2, Czech Republic
e-mail: AStastna@gmail.com

Introduction

The Krkonoše-Jizera Terrane represents one of the important quarrying areas where carbonate rocks were produced in the past. The traditional use of local marbles is already known from prehistory. The main exploitation occurred in sixteenth to eighteenth centuries when those marbles were popular for polished stonemason and sculptural applications (Rybařík 1994; Krutský 1986).

Marbles from the Jizera and Ještěd Mts were formerly used mainly for industrial applications (production of lime, cement, finely ground agricultural limestone). Raspenava (Jizera Mts) is the only locality where an exploitation of dimension stones is documented. Raspenava Marble, also known as *ophicalcite*, has been used to decorate burial chapel of Redern family in Dean Church of Frýdlant (Hladká 1955, 1957; Krutský 1993).

Determination of the source locality of marbles is a difficult task, due to common petrographic variability of stones coming from the same locality and very close petrographic, mineralogic or geochemical features of stones from different areas. In particular, there is no universal method applicable to determine the source locality. The most recent and effective approaches usually combine different analytical techniques, which is discussed in detail elsewhere (Craig and Craig 1972; Herz 1985; Barbin et al. 1992). The most widely used procedure for the identifications of sources of marbles involves a combination of petrographic, C–O stable isotope or cathodoluminescence analyses (Lapuente et al. 2000, 2002; Gorgoni et al. 2002).

Present study aims to compile petrographic and geochemical data for distinction between different types of marbles. The particular suitability and eventually limits are discussed in respect of use of experimental techniques for provenance studies. The results have implications for the proper selection of methods suitable for small samples obtained from historical monuments and for a future possible comparison of samples with historical artefacts.

Geological settings

The Krkonoše-Jizera Terrane (KJT), in the northern part of the Bohemian Massif, is currently interpreted as a Variscan NW-directed orogenic wedge, which developed between the orogenic root of the Orlica-Snieźnik lower to middle crustal complexes in the E, and autochthonous (Cadomian) Lusatian foreland to the NW (Winchester et al. 2003) (Fig. 1). Geologically very coplicated area consists of Jizera, Ještěd, Železný Brod, Krkonoše and Rýchory crystalline units. The western autochthonous part (the Lusatian Terrane, the Ješted Mountain range) is composed of the Cadomian granitoids with their end-Proterozoic country rocks that are unconformably overline with Palaeozoic rocks (Hladil et al. 2003). The allochthonous part is exposed mostly in the east (Krkonoše Mts) and formed from Palaeozoic rocks (Chlupáč et al. 2002). The Krkonoše-Jizera pluton fills the arched structure between these two parts and is composed of the Upper Variscan granites.

The carbonate formations from the west edge KJT are located in the Jizera Mts (Raspenava) and in the Ještěd Mountain range (three areas: The SE part S of Liberec, the W part and the N part). This area includes marble intercalations ranging in age from Cambrian to Devonian (Hladil et al. 2003; Winchester et al. 2003). Formerly the metamorphosed carbonates from Raspenava (Jizera Mts) were placed in Middle Proterozoic (Chaloupský et al. 1966, 1989).

From a petrographic standpoint, the metacarbonates from Raspenava (*ophicalcite*) are white and grey calcitic to dolomitic marble, rich in serpentine and metamorphosed in amphibolite-facies conditions (Hladká 1955, 1957). This locality, Raspenava, comprises lenses of marbles, erlans

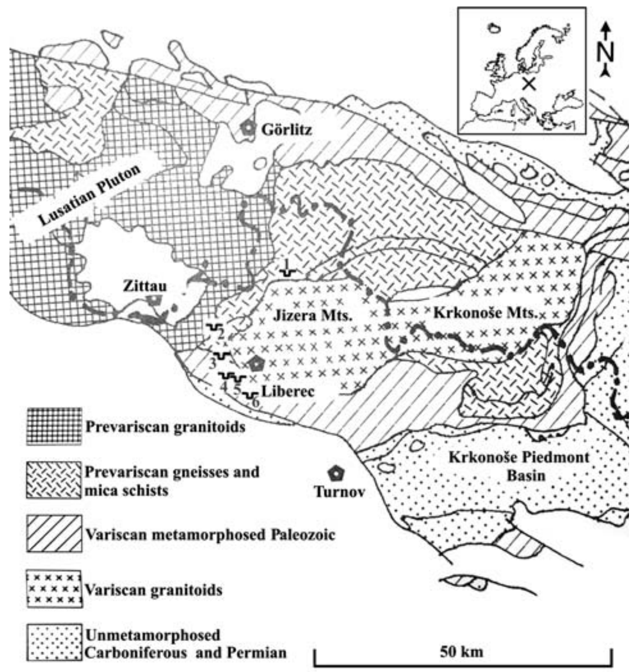

Fig. 1 A simplified geological map of the Krkonoše-Jizera Cristalline Unit (north part of the Bohemian Massif) with sampled localities in the west edge Krkonoše-Jizera Terrane (*1* Raspenava, *2* Jitrava, *3* Křižany, *4* Pilínkov, *5* Horní Hanychov, *6* Rašovka)

and amphibolites thrust into mica schists. The surrounding rocks are mica schists, the Jizera Orthogneisses and leptinites running in the form of NE–SW directed stripes from Poland to Raspenava and are then terminated by the intrusion of the Krkonoše-Jizera pluton (Chaloupský 1989). Marbles occurring in the Ještěd area are mainly graphitic, poor in dolomite (S and W parts: from Rašovka to Jitrava) or pale to dark grey dolomitic marbles (the N part: from Kryštofovo Údolí to Karlov).

The southern part of the Ještěd Mts is formed by phyllites with intercalations of Middle to Upper Devonian marbles (Chlupáč and Hladil 1992). The western unit is made up of mainly flysch deposits with intercalations of metabasalts, acidic volcanics and marbles with fauna indicating the proximity of the Devonian-Carboniferous boundary (Chlupáč et al. 2002). Lower Palaeozoic graphite phyllites with metabasite, quarzite and lenses of marbles are located in the north of the Ještěd Mountain range, ranging in age from Cambrian to Devonian (Winchester et al. 2003). The grey marbles are affected by low-grade greenschist facies; thus relics of fossils are sometimes preserved in them. Metacarbonates of the Železný Brod area appear on the east of Ještěd Mts. Local geology is represented by the Železný Brod Volcanic Complex (metamorphosed volcanics, volcanogenic quartzites and marbles) and the sericite phyllites with intercalations of marbles and quartzites and with volcanic products (Chaloupský 1989; Hladil et al. 2003).

Different types of marbles occur also in Krkonoše Mts. Hladil et al. (2003) described metamorphosed carbonates from the east edge of KJT (Krkonoše Mts) in detail. There are several areas rich in marbles like the Rokytnice, the Vrchlabí, the Maršov-Rýchory area and smaller local occurrences such as Strážné, Velká Úpa, Malá Úpa, Poniklá.

Sampling and analytical techniques

The six quarries examined in this study are located in the Ještěd and Jizera Mts, in the west edge of Krkonoše-Jizera Terrane, from N to S: Raspenava, Jitrava, Křižany, Pilínkov, Horní Hanychov, Rašovka (Fig. 1). The quarry areas were chosen on account of the literature search (Svoboda 1955; Krutský 1971, 1979, 1990, 1993; Krutský et al. 1968; Procházka 1977, 1979; Rybařík 1994). The weight of the fresh sample taken from each locality was about 20 kg; the number of samples varied according to the chromatic and fabric characteristics of the material. A total of 10 samples were collected. All studied quarries are abandoned at present.

The set of analytical methods used in this study is based on the experiences with white marbles from the Mediterranean area (compare e.g. Barbin et al. 1992; Craig and Craig 1972; Gorgoni et al. 2002), where the provenance was investigated in detail.

All samples were studied by microscopic observation of thin sections using an optical microscope Leica DMLP (Laboratory of Optical Microscopy, Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University).

X-ray diffraction (XRD) was carried out on powdered insoluble residues (determined by treatment with 1M HCl solution) using a Philips X'Pert PRO diffractometr (PW3040/60) (Laboratory of XRD, Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University). XRD analysis of magnetite (sample no 174) was carried out on powdered samples of separated fractions.

All samples were examined using the cold cathodoluminescence equipment CCl 8200 Mk4 (Laboratory of Optical Microscopy, Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University) coupled with the optical microscope Leica DMLP. The electron energy applied to the thin sections was 14–15 kV, and the beam current was operated at 320–350 μA. The luminescence colours of each lithotype have been photographed with the Olympus C-2000 camera with a long exposure time. This cathodoluminescence was corroborated by thin-section microscopy with the aid of a staining technique (Dickson and Piotrovskij methods to distinguish Fe–calcite and calcite from dolomite) in three cases (Pilínkov, Horní Hanychov, Jitrava rose type), because of very faint to non-luminiscence of these samples. These staining methods are described in detail elsewhere (Miller 1988).

Carbon and Oxygen isotope analysis of carbonates were performed using conventional reaction with 100% H_3PO_4 under vacuum with a Finningan MAT 251 isotope ratio mass spectrometer (Laboratory of Stable Isotopes, Czech Geological Survey). Overall analytical precision was ±0.1‰. For those, containing dolomite (sample no 174 B I, 174 D I), the $\delta^{18}O$ values were corrected by subtraction of 0.84‰ from measured values. The results were expressed in the form of usual δ‰ units against PDB.

The bulk magnetic susceptibility was measured with the aid of the Kappabridge KLY-4 equipment, AGICO Ltd. laboratory in Brno.

Results and discussion

Mineralogy and petrography

The samples from the Jizera district can be characterised as dolomitic marbles which can be divided into two distinct types. The medium-grained dolomitic marbles (white type) contain green serpentine veins and high content of calcite and accessory minerals. The second type is distinguishable by its fine grain size, serpentine content and the poor abundance of calcite and accessory minerals (white and grey type with graphitic content). The samples from the Ještěd Mts are pure calcite marbles with the exception of those from Horní Hanychov in which dolomite is abundant (~10 vol%). Remarkable characteristics are their fine grain size and graphitic content. All these grey marbles are similar to each other and include white calcite veins except the two, one from Jitrava (rose type) and the dark grey to black marble with calcitic veins (randomly oriented) from Rašovka. The compact marbles from the Jizera Mts (Raspenava) show polygonal fabric except the grey type, that exhibits pronounced lineation. The majority of marbles from the Ještěd Mts display linear fabric along the graphitic strips. Mineralogical composition based on optical microscopy of all studied samples is summarised in Table 1.

Although carbonates represent the dominant phases in the studied rocks, the content of insoluble residues (2–11 wt% with about 8 wt% as average) is also significant (Table 2). Two of studied samples (sample no 174 C, 241 B) show more than 10 wt% of non-carbonate phases; the remaining marbles are rather poor in accessory minerals. The XRD results on the insoluble residues revealed a mineralogical composition made up of clinochlore, serpentine, tremolite, diopside, pyrite and magnetite in the locality Raspenava. Clinochlore, muscovite, quartz, pyrite,

Table 1 The mineralogical composition of the studied samples obtained from optical microscopy

Quarry	S. no.	Calcite	Dolomite	Quartz	Muscovite	Mg chlorite	Tremolite	Diopside
Raspenava white	174 A	+++	+++	–	–	+	–	–
	174 B	+++	+++	–	–	+	+	–
	174 C	+++	+++	–	–	+	++	+
Raspenava grey	174 D	++	+++	–	–	+	++	–
Jitrava rose	241 A	+++	–	+	+	+	–	–
Jitrava grey	241 B	+++	–	+	–	–	–	–
Křižany	132	+++	–	++	+	+	–	–
Pilínkov	243	+++	–	++	++	–	–	–
Horní Hanychov	244	+++	++	+	+	–	–	–
Rašovka	204	+++	–	+	+	+	–	–

Quarry	S. no.	Serpentine	Forsterite	Limonite	Haematite	Pyrite	Magnetite	Graphite	Rutile
Raspenava white	147 A	++	–	–	–	+	+	–	–
	174 B	++	–	+	–	+	+	–	–
	174 C	++	+	–	–	+	+	–	–
Raspenava grey	174 D	++	–	–	–	+	+	+	–
Jitrava rose	241 A	–	–	+	+	–	–	+	–
Jitrava grey	241 B	–	–	–	–	+	–	+	–
Křižany	132	–	–	–	–	–	–	+	–
Pilínkov	243	–	–	–	–	+	–	+	+
Horní Hanychov	244	–	–	+	–	+	–	+	+
Rašovka	204	–	–	+	+	+	–	+	–

+++ very abundant, ++ abundant, + present, – not observed

Table 2 Average values of insoluble residues (determined by treatment with 1M HCl solution) and mass of soluble carbonates in percentage by weight

Quarry	S. no.	Insoluble residues [wt%]	Mass of soluble carbonates [wt%]
Raspenava white	174 A	8.6	91.4
	174 B	2.1	97.9
	174 C	11.0	89.0
Raspenava grey	174 D	9.0	91.0
Jitrava rose	241 A	9.5	90.5
Jitrava grey	241 B	10.7	89.3
Křižany	132	8.4	91.6
Pilínkov	243	9.8	90.2
Horní Hanychov	244	1.7	98.3
Rašovka	204	5.5	94.5

rutile and haematite were found in the marbles from Ještěd Mts. The main disadvantage of XRD analysis on insoluble residues is the high material consumption along the carbonates leaching, which is unsuitable for historical artefacts.

Isotopic signature

The stable isotopic composition of metacarbonates is controlled by four factors: (1) the mode of origin; (2) the effect of volatilization; (3) the exchange with infiltrating fluids; (4) the temperature of exchange (Valley 1986).

The δ^{13}C and δ^{18}O values of unmetamorphosed carbonate rocks of Upper Proterozoic and Palaeozoic age range from –5 to +4‰ and from –8 to 0‰ (PDB), respectively (Jacobsen and Kaufman 1999; Veizer et al. 1999). The δ^{13}C and δ^{18}O data of the groundmass of fresh samples from the west edge Krkonoše-Jizera Terrane ranges from –1 to +3‰ and from –8 to –20‰, respectively. The δ^{13}C and δ^{18}O values of late carbonate veins decrease to –3‰ and reach more negative values up to –26‰ in case of δ^{18}O. All values are relative to PDB. The whole carbon and oxygen isotopic data are displayed in Table 3.

Stable isotopic geochemistry distinguished the genetically different carbonate of the groundmass from the secondary calcite in veins. The isotopic shifts in secondary veins of the studied marbles are most likely caused by exchanges with metamorphic or magmatic fluids, the lower δ^{18}O value of the calcitic vein from Jitrava (sample no 241 B II, Ještěd Mts) may be due to interaction with meteoric

Table 3 Isotopic signature of the marbles from the west edge *KJT*

Quarry	S. no.	δ^{13}C (‰, PDB)	δ^{18}O (‰, PDB)
Raspenava	174 A I	–1.01	–19.49
	174 B I	1.18	–18.09
	174 C I	3.08	–19.84
	174 D I	3.04	–18.08
	174 D II	0.80	–18.37
Jitrava	241 A I	2.65	–11.51
	241 B I	–0.36	–12.46
	241 B II	–2.55	–25.63
	241 B III	–2.02	–8.70
Křižany	132 I	2.41	–8.74
	132 II	2.26	–8.71
Pilínkov	243 I	1.76	–10.30
	243 II	1.49	–9.68
	243 III	–1.25	–15.57
Horní Hanychov	244 I	2.61	–9.05
	244 II	2.56	–9.28
Rašovka	204 I	0.61	–9.47
	204 II	0.97	–10.17

KJT Krkonoše-Jizera Terrane

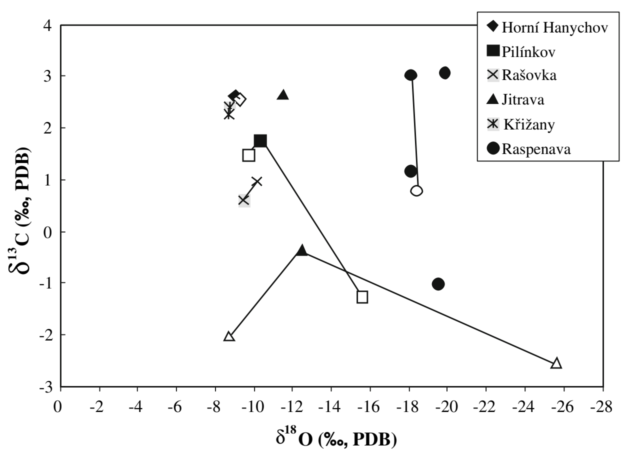

Fig. 2 Plot of δ^{13}C versus δ^{18}O for all samples studied in this work. *Tie-lines* connect the data point of the groundmass with that of the vein(s) of the same sample, if present. The *filled symbols* represent groundmass, the *empty signs* picture carbonate veins with different orientation in regard of the foliation

waters (Fig. 2). The studied samples fall into two groups: marbles from Raspenava with oxygen isotopic shifts to lower δ-values than marbles from the Ještěd Mts. The larger decrease of δ^{18}O in methacarbonates from Raspenava can be explained by higher grade of metamorphism (amphibolite facies). The carbon isotopic compositions of all studied samples fall into the field of normal marine sedimentary carbonates of Upper Proterozoic and Palaeozoic age.

For most of the studied localities, the information on isotopic composition of marbles was missing. Previous studies focused on the stable isotopic characteristics of marbles from the Krkonoše Mts (Strážné-Hříběcí Boudy and Malá Úpa), Železný Brod crystalline unit and the surrounding (Koberovy, Jesenný, Křížlice), Ještěd Mts (Padouchov) and Jizera Mts (Raspenava) in the unpublished report (Hladíková et al. 1989). These δ^{13}C and δ^{18}O data of carbonate phases from marbles from the Železný Brod crystalline unit are similar to those from the Ještěd Mts (both greenschist facies) and also the values from Raspenava correlate with each other (Fig. 3). Samples from Strážné (Krkonoše Mts) exhibit similar δ^{18}O depletions as those from Raspenava (Jizera Mts), which is probably connected with the conformable higher grade of metamorphism (invasion of low δ^{18}O fluids during metamorphism).

Isotopic analysis requires only minute quantities of material, which is the main advantage of this method. The variation of δ^{13}C and δ^{18}O in samples (e.g. differences between isotopic composition of groundmass and secondary veins) represents the major restriction of the use of isotopic analysis in source determination. This concerns mainly minute samples taken from small artefacts where the groundmass is undistinguishable from veins.

Cathodomicrofacies

The different colours of luminescence depend on impurities in the crystal or on lattice defects (Barbin et al. 1992). Cathodoluminescence (CL) in carbonates is mainly caused by trace elements presented by activators (Mn^{2+}, Sm^{3+}, Tb^{3+}, Dy^{3+}, Eu^{3+} etc.), sensitizers (Pb^{2+}, Ce^{3+} etc.) and quenchers (Fe^{2+} ,Fe^{3+}, Ni^{2+}, Co^{2+} etc.) (Machel 2000). The ratio Mn^{2+}/Fe^{2+} is also important. A Mn:Fe ratio higher than 2:1 is typical for calcite with intensive luminescence, but if this ratio is less than 1:3, luminescence becomes weak (Yardley and Lloyd 1989). Marbles show luminescence in a relatively broad range of colours, that depends on many factors, mainly not only because of chemical composition but also because of the type of equipments used for measuring CL properties.

The studied marbles from the west edge Krkonoše-Jizera Terrane show orange to reddish brown luminescence of carbonates. Accessory minerals and non-carbonate phases (serpentine, tremolite, forsterite, opaque minerals) are non-luminescent or display very dull luminescence (quartz) in comparison with carbonates. The properties of the studied microfacies are summarised in Table 4.

Dolomite–calcite marbles from the Jizera Mts (Raspenava) can be clearly identified from their cathodomicrofacies. Their fabric is dominated by homogeneous calcite (orange CL) and

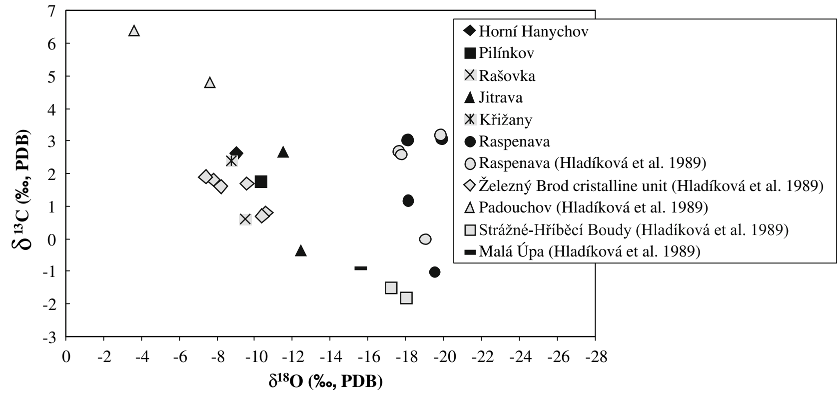

Fig. 3 Comparison of stable isotope data from this study with data from Hladíková et al. (1989). The values considered here are related to the groundmass

Table 4 Main attributes of cathodomicrofacies from the studied area

Quarry	S. no.	Diametral grain-size (mm)	Marble	Cathodoluminescence		
				Colour	Intensity	Distribution
Raspenava white	174A	0.1–1	Calcite + dolomite	Pale and dark orange, reddish brown	Strong	Homogeneous, two generations of calcite
	174B	0.1–1	Dolomite + calcite	Reddish brown, orange	Strong	Homogeneous
	174C	0.1–1	Calcite + dolomite	Orange, reddish brown	Strong	Homogeneous
Raspenava grey	174D	0.1–0.5	Dolomite + calcite	Reddish brown, orange	Strong	Homogeneous
Jitrava rose	241A	0.05–0.1	Calcite	Dark orange, brown	Faint, medium–strong in veins	Homogeneous
Jitrava grey	241B	0.1–0.5	Calcite	Orange	Medium, strong in veins	Zoned grains, homogeneous
Křižany	132	0.1–2	Calcite	Pale and dark orange, black quartz	Medium–strong	Inhomogeneous, two generation of calcite
Pilínkov	243	0.3–1	Calcite	Dark orange, red to brown	Very faint	Inhomogeneous, patchy
Horní Hanychov	244	0.1–0.5	Calcite + dolomite	Dark orange, red to brown	Very faint	Inhomogeneous, patchy
Rašovka	204	0.2–0.5	Calcite	Orange, dark brown	Faint-strong	Zoned in veins, orange limits

The diametral grain-size refers to carbonate grains (calcite, dolomite); the intensity and the distribution are obtained from CL microscopy (not measured)

isolated dolomite grains (dark red to reddish brown CL). Marbles from Raspenava were separated within two groups: first one, where the reddish brown luminescence of dolomite is dominant (sample no 174 B, 174 D) (Fig. 4a) and second one, where calcite with the orange luminescence prevails over dolomite (sample no 174 A, 174 C) (Fig. 4b). Two genetically different calcites are present here (pale and dark orange CL). The late calcite veins of this quarry display intensive orange luminescence, sometimes with non-luminescent opaque minerals inside (sample no 174 D) (Fig. 4a). Forsterite is preserved or often completely serpentinized; in both cases shows no-luminescence. Tremolite and opaque minerals are also non-luminescent.

Calcitic marbles from the Ještěd Mts show an orange luminescence in a broad range of tints. Marbles from the southern part of the Ještěd Mts (Horní Hanychov and Pilínkov) display superiority of quenchers, mainly Fe-enriched calcite (proved by staining techniques). According to recent findings (Cazenave et al. 2003), only manganese contributes to orange CL of carbonates. Based on our results supported by staining techniques, the faint luminescence of these samples is due to the Fe-enriched calcite. The amount of Fe (or Mn) has not been, however, quantified. Only late calcite veins show intensive orange luminescence. Opaque minerals and quartz exhibit no luminescence and very dull luminescence, respectively. Among the carbonate rocks from southern part of the Ještěd Mts, Rašovka marble can be clearly identified by its distinct CL fabric. Primary calcite in groundmass exhibits a dark orange to brown luminescent colour with intense orange luminescent limits, which looks like a spreading web (Fig. 4c). The secondary calcite veins are often

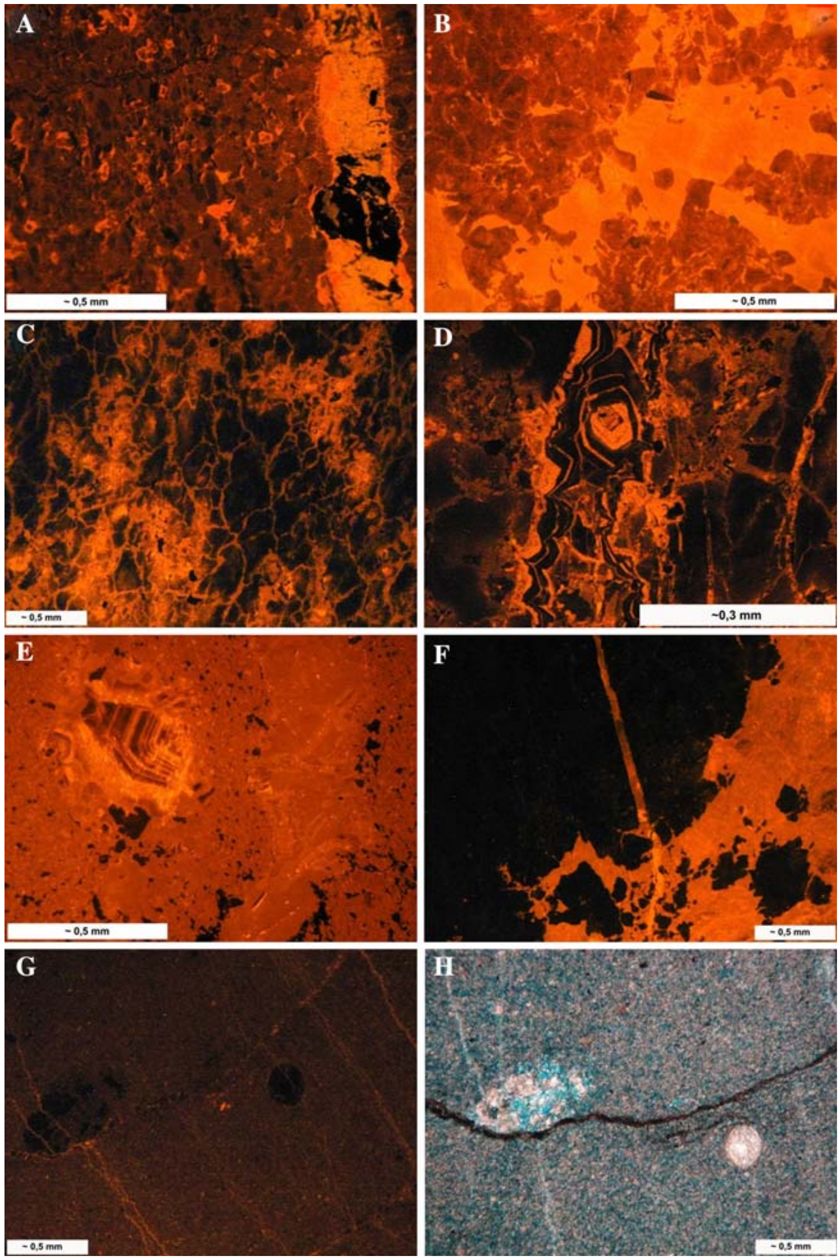

Fig. 4 Cathodoluminescence microscopy of the studied marbles. **a** CL image of dolomite-calcite marble from Raspenava (Sample No 174 D, Jizera Mts.). The secondary calcite vein with an intense orange luminescence (bright grey in black and white) and non-luminescent pyrite within. Dolomite with a reddish brown luminescence (dark grey in black and white) prevails over orange luminescence calcite (bright grey in black and white). **b** CL image of calcite-dolomite marble from Raspenava (Sample No 174 A, Jizera Mts.). Isolated dolomite grains exhibit a dark red to reddish brown luminescence (dark grey in black and white), dominant calcite shows a homogeneous orange colour (bright grey in black and white). **c** CL image of calcite marble from Rašovka (Sample No 204, JeštědMts.). The characteristic fabric consists of a dark orange to brown luminescence calcite (dark grey in black and white) with intense orange luminescence limits (bright grey in black and white) (similar to a spreading web). **d** CL image of calcite marble from Rašovka (Sample No 204, Ještěd Mts.). The oscillatory zoning of calcite grains occur in a secondary calcite vein (a rotation of light and dark CL zones). **e** CL image of calcite marble from Jitrava, the grey type (Sample No 241 B, Ještěd Mts.). The oscillatory zoning of a calcite grain in the groundmass. Small pyrite grains are non-luminescent, quartz shows very dull luminescence, a secondary calcite vein exhibits an orange luminescence (bright grey in black and white). **f** CL image of calcite marble from Křižany (Sample No 132, Ještěd Mts.). A secondary calcite vein (intense orange luminescence, bright grey in black and white) penetrates the quartz grain (black). **g** Cl image of calcite marble from Jitrava, the rose type (Sample No 241 A, Ještěd Mts.). The relics of fossils show very faint (Fe-calcite) to very dull luminescence (quartz). **h** Calcitemarble from Jitrava, the rose type (Sample No 241 A, Ještěd Mts.). The microphotograph of a thin section obtained by the staining technique (the Dickson method). A sections of a spicule of sponges (sphere) is silicified (quartz is achromatic). The relics of Brachiopoda (oval) are partly calcified (blue Fe-calcite, grey in black and white) and silicified, respectively. The fine-grained calcite of the groundmass is Feenriched (blue colour, grey in black and white)

oscillatory zoned (a rotation of light and dark zones) (Fig. 4d). Each zone is 5 to 30 µm wide. Similarly to this oscillatory zoning, isolated calcite grains, that were found in the groundmass in grey marbles from Jitrava (the western part of the Ještěd Mts), are also zoned (dark cores and light rims) (Fig. 4e). These zones are 10 to 40 µm wide and are crowded toward the centre of the grain. The rose variety of marble from Jitrava displays a dark orange to brown luminescence of the fine-grained Fe–calcite and more intense orange luminescence of late calcite veins. Jitrava is the only locality, where relics of fossils were preserved. The grey and rose varieties of this marble contain spherical non-luminescent grains, 0.2–0.5 mm wide (Fig. 4g). These grains are probably sections of a spicule of sponges, which could be silicified. Brachiopoda, another preserved fossil, are present in both types of marbles from Jitrava. Based on microscopic feature, they were probably partly calcified (Fe–calcite) and silicified, respectively (Fig. 4h). The graphitic marble (grey type) includes shell fragments of thin-walled pelecypods (P. Budil, personal communication). All relics of fossils show a very faint to no luminescence.

Marbles from Křižany (the western part of the Ještěd Mts) exhibit a deep orange homogeneous luminescence with isolated grains of quartz (black CL), which are sometimes crosscutted by intense luminescent late orange calcite veins (Fig. 4f). The isolated grains of a genetically different calcite display pale orange luminescence.

The accessory minerals (muscovite, clinochlore, haematite, limonite, graphite, pyrite) from the Ještěd Mts marbles are usually non-luminescent. The isolated grains or incrustations are spread in a groundmass or are accumulated in veins.

Cathodoluminescence is a powerful inexpensive complementary microscopic method allowing more precise distinction among marbles with variable composition. Along with its sensitivity to the variation in chemical composition of carbonates, it also facilitates distinction of fossil fragments that are not visible by conventional microscopy. This contributes to separation of marbles by microfacial analysis, a technique proposed for provenance studies by Flügel and Flügel (1997).

Magnetic characteristics

Summary values of the bulk magnetic susceptibility are set out in Table 5. The anomalous values of samples from Raspenava are caused by presence of magnetite. The increased values of marbles from Jitrava and Pilínkov are due to paramagnetic minerals (pyrite, Mg chlorite).

The most suitable marbles conducive to decorative purposes are diamagnetic (calcite > dolomite marbles from Horní Hanychov, Ještěd Mts). If magnetite is abundant, there is a risk for rusting if the stone is exposed to atmospheric conditions (Winkler 1997). The bulk magnetic susceptibility measurement represents useful additional method for provenance studies, when marbles with different magnetic characteristics are compared. The majority of pure white marbles is diamagnetic, and therefore this method based on physical properties of samples is redundant for them.

Table 5 Magnetic characteristics of marbles from the west edge *KJT*, k presents the bulk magnetic susceptibility [SI] [a]

Quarry	S. no.	k1 [10^{-6}]	k2 [10^{-6}]	kmean [10^{-6}]
Raspenava white	174A	28.4	28.5	28.4
	174B	392.0	393.0	392.0
	174C	297.0	280.0	280.0
Raspenava grey	174D	773.0	774.0	774.0
Jitrava rose	241A	187.0	183.0	185.0
Jitrava grey	241B	45.3	45.4	45.4
Křižany	132/1	3.0	3.0	3.0
	132/2	5.8	5.9	5.9
	132/3	0.5	0.4	0.5
Pilínkov	243	31.6	31.8	31.7
Horní Hanychov	244/1	–6.1	–6.2	–6.2
	244/2	0.5	0.4	0.5
Rašovka	204/1	3.4	3.6	3.5
	204/2	4.7	4.8	4.8

KJT Krkonoše-Jizera Terrane

Conclusions

Marbles from six quarries of the West edge of the Krkonoše-Jizera Terrane were investigated to evaluate the potential of different analytical methods for provenance studies of these rocks.

Marbles from the Jizera Mts (Raspenava) are distinguished by green serpentine veins, and two types of methacarbonates: the mid-grained calcite–dolomite marbles (white type) and the fine-grained dolomitic marbles with a lower calcite content (white and grey type). The studied carbonate grains show mainly different tints of an orange homogeneous luminescence of calcite grains; on the other hand isolated dolomite grains exhibit a dark red to reddish brown luminescence. Moreover, the marbles from Raspenava mainly show a polygonal fabric. The mineralogical composition of the insoluble residues is highly variable and consists of clinochlore ± serpentine ± tremolite ± diopside ± pyrite + magnetite. Carbon and especially oxygen isotopic data are very significant and permit quarry separation in this case: the $\delta^{13}C$ and $\delta^{18}O$

values of carbonates range from –1 to +3‰ and from –18 to –20‰ (PDB), respectively. Samples of this quarry display increased values of the bulk magnetic susceptibility due to the magnetite content.

The grey calcite marbles from the Ještěd Mts (Jitrava, Křižany, Pilínkov, Horní Hanychov, Rašovka) are fine-grained and penetrated by white late calcite veins, which are differently oriented with regard to the foliation. These samples mainly exhibit linear fabric and include graphitic matter. The mineralogical composition of the insoluble residues is also very variable and consists of clinochlore + muscovite ± quartz ± pyrite ± rutile ± haematite. Stable isotope analyses of carbonates in the groundmass and genetically different secondary veins proved that C and O isotope data can vary significantly within one sample. Low δ^{18}O values of several calcite veins suggest invasion of low δ^{18}O fluids of metamorphic or magmatic origin or else meteoric origin in case of the sample from Jitrava. The δ^{13}C and δ^{18}O values of carbonates range from 0 to +3‰ and from –9 to –26‰ (PDB), respectively. Jitrava is also the only locality, where relics of fossils are observed (spicule of sponges, brachiopoda and thin-walled pelecypods). Oscillatory zoning was found in calcite with the aid of cathodoluminescence in two samples (Jitrava and Rašovka). Marbles from Pilínkov, Horní Hanychov and Jitrava (rose type) exhibit a very faint luminescence; the remaining marbles display differently distributed tints and intensities of the orange calcite luminescence. The majority of marbles from the Ještěd Mts has a low bulk magnetic susceptibility.

For provenance studies the most important factors are (a) the amount of a sampled material from historical artefacts and (b) the sort of analytical techniques and their predicative ability. The results obtained indicate that the most effective and discriminant way to search for the origin of marbles is the combination of petrographic methods with the cathodoluminescence and with the stable isotope analysis. The bulk magnetic susceptibility measurement represents a useful additional method for provenance studies in the case of comparison of marbles with different magnetic characteristics. Methods based on insoluble residues (e.g. XRD analysis) are inapplicable because of a high demand of material and a variable mineral content.

Acknowledgments Work carried out with financial support by the Czech Ministry of Education (the project MSM 520000001 and MSM 0021620855).The authors are grateful to Wali Shah Faryad for the assistance in optical microscopy, to Karel Žák for measuring and interpretation of the stable isotopes, to Marta Chlupáčová for the bulk magnetic susceptibility measurement, to Petr Budil for help with interpretation of relics of fossils, to Marie Fayadová for help in the geochemical laboratory of the Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University.

References

Barbin V, Ramseyer K, Decrouez D, Burns SJ, Chamay J, Maier JL (1992) Cathodoluminescence of white marbles: an overview. Archaeometry 34:175–183

Cazenave S, Chapoulie R, Villeneuve G (2003) Cathodoluminescence of synthetic and natural calcite: the effects of manganese and iron on orange emission. Mineral Petrol 78:243–253

Chaloupský J (1989) General geological map of Krkonoše and Jizera Mts. 1:100000. Ústř Úst geol, Prague

Chaloupský J, Domečka K, Klomínský J, Králík F, Líbalová, Opletal M, Pošmourný K, Sattran V, Sekyra J, Tonika J (1966) Final report about the project 1/02 and basic geological research on the Krkonoše-Jizera Crystalline Unit (in Czech). Unpublished report, MS Geofond Prague

Chlupáč I, Hladil J (1992) New Devonian occurrences in the Ještěd Mts., North Bohemia. ČMG 37:185–191

Chlupáč I, Brzobohatý R, Kovanda J, Stráník Z (2002) Geological history of the Czech Republic (in Czech). Academia, Prague, 436 pp

Craig H, Craig V (1972) Greek marbles: determination of provenance by isotopic analysis. Science 176:401–403

Flügel E, Flügel C (1997) Applied microfacies analysis: provenance studies of Roman mosaic stones. Facies 37:1–48

Gorgoni C, Lazzarini L, Pallante P, Turi B (2002) An updated and detailed mineropetrographic and C–O stable isotopic reference database for the main Mediterranean marbles used in antiquity. In: Hermann JJ Jr, Herz N, Newman R (eds) Asmosia 5. Interdisciplinary studies on ancient stone. Archetype Publications, London, pp 115–131

Herz N (1985) Isotopic analysis of marble. In: Rapp G Jr, Gifford JA (eds) Archeological geology. Yale University Press, New Haven, pp 331–351

Hladil J, Patočka F, Kachlík V, Melichar R, Hubačík M (2003) Metamorphosed carbonate sediments of the Krkonoše Mts. and Palaeozoic evolution of Sudetic terranes (NE Bohemia, Czech Republic). Geol Carpathica 54:281–297

Hladíková J, Mrázek P, Žák K (1989) Carbon and oxygen isotopic compositions of carbonate rocks from the Czech Republic and Moravia (in Czech). Unpublished report Ústř Úst geol Prague

Hladká N (1955) Mineralogical-petrographic conditions in the Vápenný Vrch near Raspenava and its wider surrounding (in Czech). MSc Thesis, Charles University, Prague

Hladká N (1957) Mineralogical-petrographic conditions in the Vápenný Vrch near Raspenava and its wider surrounding (in Czech). Sbor Ústř Úst Geol Odd Geol 24:169–207

Jacobsen SB, Kaufman AJ (1999) The Sr, C and O isotopic evolution of Neoproterozoic seawater. Chem Geol 161: 37–57

Krutský N (1971) Marbles from Krkonoše-Jizera Teranne and their geological treatment and industrial exploitation after the year 1945 (in Czech). Opera corcontica 7(8):19–36

Krutský N (1979) Prospecting results in carbonate deposits from the Krkonoše Crystalline Unit (in Czech). Sborník 22. Konference ČSMG, Trutnov, pp 83–94

Krutský N (1986) From the History of mining and exploitation of limestones in ČSR (in Czech). In: Kužvart M (ed) Historie využití nerud. Sborník přednášek semináře 32. Fora pro nerudy, NTM Praha, 12.11.1985, Prague, pp 70-79

Krutský N (1990) The raw material study. North Bohemian region—limestones for the agricultural industry (in Czech). Unpublished report, MS Geofond Prague

Krutský N (1993) From the History of stones mining and exploitation in the Northen Bohemia (in Czech). Geol Průzkum 35:261–264

Krutský N, Čtyroký V, Cmuntová M, Růžička T (1968) Final report. Marbles from the Krkonoše Mts. The raw material: marble (in Czech). Unpublished report, MS Geofond Prague
Lapuente MP, Turi B, Blanc P (2000) Marbles from Roman Hispania: stable isotope and cathodoluminescence characterization. App Geochem 15:1469–1493
Lapuente MP, Martinez MP, Turi B, Blanc P (2002) Characterization of dolomitic marbles from the Malaga Province (Spain). In: Hermann JJ Jr, Herz N, Newman R (eds) Asmosia 5. Interdisciplinary studies on ancient stone. Archetype Publications, London, pp 152–162
Machel HG (2000) Application of cathodoluminescence to carbonate diagenesis. In: Pagel M, Barbin V, Blanc P, Ohnenstetter D (eds) Cathodoluminescence in geosciences. Springer, Heidelberg, pp 271–301
Miller J (1988) Microscopical techniques: slices, slides, stains and peels. In: Tucker M (ed) Techniques in sedimentology. Blackwell, Oxford, pp 99–100
Procházka J (1977) Prospecting results in marbles from the Krkonoše-Jizera terrane (in Czech). Sbor Geol Věd LG-M 18:161–197
Procházka J (1979) Marble deposits in the Krkonoše Crystalline Unit (in Czech). Sborník 22. Konference ČSMG, Trutnov 1979, pp 95–101
Rybařík V (1994) Dimension stones from the Czech Republic (in Czech). Nadace Střední průmyslové školy kamenické a sochařské v Hořicích v Podkrkonoší, 218 pp
Svoboda J (1955) Limestones from the Krkonoše and Jizera Mts. (in Czech). Geotechnica, 21, Praha, pp 1–67
Valley JW (1986) Stable isotope geochemistry of metamorphic rocks. In: Valley JW, Taylor HP Jr, O'Neil JR (eds) Stable isotopes in high temperature geological processes. Rev Miner 16:445–489
Veizer J, Ala D, Azmy K, Bruckschen P, Buhl D, Bruhn F, Carden GAF, Diener A, Ebneth S, Godderis Y, Jasper T, Korte Ch, Pawellek F, Podlaha OG, Strauss H (1999) $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ evolution of Phanerozoic seawater. Chem Geol 161:59–88
Winchester JA, Kachlík V, Patočka F, Mezer M, Nawakowski C, Crowley QG, Floyd PA (2003) Geochemistry of metasedimentary sequences in the Krkonoše-Jizera Terrane, West Sudetes, Bohemian Massif: Palaeotectonic and stratigraphic implications. J Czech Geol Soc 48:135–136
Winkler EM (1997) Stone in architecture. Properties, durability, 3rd revised edn. Springer, Berlin, 313 pp
Yardley BWD, Lloyd GE (1989) An application of cathodoluminescence microscopy to the study of textures and reactions in high grade marbles from Connemara, Ireland. Geol Mag 126:333–337