## Application of cathodoluminescence to the study of metamorphic textures in marbles from the eastern part of the Bohemian Massif

Stanislav Houzar<sup>1</sup> – Jaromír Leichmann<sup>2</sup>

<sup>1</sup> Moravian Museum, Department of Mineralogy and Petrography, Zelný trh 6, 659 37 Brno, Czech Republic. E-mail: shouzar@mzm.cz
<sup>2</sup> Masaryk University, Institute of Geological Sciences, Kotlářská 2, 611 37 Brno, Czech Republic. E-mail: leichman@sci.muni.cz

Abstract. Application of cathodoluminescence to the marble study opens new possibilities in the investigation of metamorphic reaction textures and mineral assemblages in marbles in comparison to the observation using transmitted light. The CL study of marbles in the Moravicum and Moldanubicum units indicated that, with an increasing grade of metamorphism, the CL properties of calcite, dolomite and some other minerals change depending on the mineral reactions and chemical composition. Photographs illustrate examples of different textures and CL of minerals from the studied units, representing marbles of different metamorphic grades from the greenschist facies (biotite zone of the Lukov Unit of the Moravicum) to the granulite facies (Moldanubicum). Structures resulting from the reactions do not always perfectly correspond with the theoretical presumptions and can be explained by a migration of components (e.g., Mg and Si) for a short distance.

Key words: cathodoluminescence microscopy, marbles, metamorphic textures, Moravicum, Moldanubicum

#### Introduction

Calcite- and dolomite-bearing rocks belong to the most often studied objects by cathodoluminescence (CL) due to their relatively intense luminescence resulting from sample bombardment by accelerated electrons. Natural calcite and dolomite show luminescence in quite a broad range of intensities and colours, ranging from purple through blue, green, white, and orange to red (Habermann et al. 1996, Marshall 1988). Luminescence is caused by defects in a crystal structure of a mineral. The most common ones, responsible for the effect of luminescence, are entrance of some atoms (so called activators) in the crystal structure and irregularities in the bonds between particular atoms. The principal activator in the case of calcite and dolomite is substitution CaMn<sup>-1</sup>. Habermann et al. (1996) disclosed that other important activators may be REE, mainly Sm<sup>3+</sup>, Dy<sup>3+</sup>, Tb<sup>3+</sup> and Eu<sup>3+</sup>. Luminescence of a particular grain of calcite or dolomite is usually not activated only by a single element, but it is caused by a combination of a dominant luminescence caused by Mn<sup>2+</sup> and a less prominent luminescence caused by the presence of REE (Habermann et al. 1996). Another factor, playing a role in the final intensity of luminescence, is the presence of atoms restraining luminescence (so-called quenchers). The most important quencher is Fe<sup>2+</sup>. This is the reason why carbonates with a high content of Fe<sup>2+</sup> in their structures do not usually show any luminescence. The ratio Mn<sup>2+</sup>/Fe<sup>2+</sup> is also important. Intense luminescence is typical for calcite with a Mn : Fe ratio higher than 2:1. When this ratio is less than 1:3, luminescence becomes weak (Yardley and Lloyd 1989).

Cathodoluminescence has been widely used in petrographical studies of sedimentary and hydrothermal carbonates (Marshall 1988, Machel 2000, Haberman et al. 2000). CL study brings good results in distinguishing calcite from dolomite and also in the identification of particular generations of carbonates. It has been used in studies of the cement, zoning of the crystals and in the identification of fossils. Wider application of this method in studies of metamorphic carbonates has only begun. Originally it was thought that luminescence of marbles will be pretty uniform (Marshall 1988). However, recent studies (Yardley and Lloyd 1989, Schmid and Ramseyer 1996, Gross et al. 1999) showed that this method is well applicable also to marbles. Similarly to sedimentary carbonates, CL enables to identify some textures in marbles, invisible under optical microscope (Plate I, 1–8).

Yardley and Lloyd (1989) studied dolomite marbles with admixture of silicates metamorphosed in the higher amphibolite facies, and distinguished a whole array of textures, originating in a reaction of dolomite and quartz resulting in the formation of tremolite and calcite. Application of CL also enabled to distinguish secondary microtextures that originated by retrograde carbonatization of tremolite. Schmid and Ramseyer (1996) used CL for the identification and interpretation of relict textures, originally of sedimentary origin, which were preserved during contact metamorphism of Permian and Triassic limestones; relicts of originally sedimentary textures identifiable by CL could survive up to approximately 400 °C. Combined CL-EMS study of dolomite marbles conducted by Gross et al. (1999) identified textures resulting from a hydrothermal alteration of original metacarbonates, caused by circulation of iron-rich fluids.

### Experimental

The Simon-Neuser cathodoluminescent microscope with a hot cathode of a HC2-LM type was used; the acceleration

voltage of the electron beam was 14 keV, current density of  $10 \ \mu\text{A/mm}^2$ . This instrument enables to observe a sample and to photograph it as in a transmitted light (TrL) or with a CL in use without a need for changing the sample or changing the field of observation. Sample used in such an observation is the same polished thin section, covered by graphite as in case of EMP analysis. About 50 samples were studied with exposure times between 10 and 30 s. Photographs were taken by the Nikon HFX automatic photographic equipment on Ektachrome 400 and Fujichrome 800.

# Geological setting and regional metamorphic characteristics of marble studied

We have studied marbles from the eastern part of the Bohemian Massif along large-scale thrusting of the Moldanubian



Fig. 1. A sketch map of western Moravia showing the geological situation of the studied localities.

crosses = magmatites, square = Lukov Unit, triangle = Vranov–Olešnice Units, circle = Moldanubicum (Varied Unit), point = Moldanubicum (Gföhl Unit). high-grade complex over the Moravian Zone and in the area west of the Třebíč durbachite massif (Fig. 1). The antiformal structure of the Moravian Zone (Dyje and Svratka Dome) is formed by a nappe composed of Cadomian Bíteš orthogneiss and metapelites with marbles and quartzites. Metasedimentary marble-bearing sequences are subdivided into the lower Lukov-Bílý Potok Unit (1) and Vranov–Olešnice Unit. An equivalent to the Vranov–Olešnice Unit of the Moravicum is the Velké Vrbno Unit (mainly its Graphite Formation) in the western part of the Silesicum. Metamorphic evolution is characterized by a Barrovian-type metamorphism generally increasing from the east towards the Moldanubian boundary in the west (Höck 1975, 1995, Mísař 1995). The metamorphic grade mostly reaches the garnet zone (Konopásek et al. 2002).

### (1) Lukov Unit

The Lukov Unit (Batík 1984), called the Pernegg Formation in Austria (Höck 1975), is characterized by calcite marbles very rich in silicates with gradual transitions to calcite and dolomite-calcite mica schists. They are located within metapelites, which are metamorphosed up to a staurolite zone in the centre of the dome. Mineral assemblage of these metapelites is quartz + muscovite + staurolite + almandine + biotite, maximum PT conditions were determined at 580-600 °C and 500-700 MPa (Höck et al. 1991). The PT conditions at the Čížov locality in the centre of the zone were calculated at 520 °C and 500-700 MPa (Pivnička 1995). The metamorphic intensity decreases towards the N and S (Höck 1995). Metamorphic conditions at Horní Dunajovice, located in the northernmost part of the unit, reached only the biotite zone. Bernroider (1989) studied mineral assemblages in marbles of the Pernegg Formation. He assumed a low  $X_{CO2}$  in the range between 0.16–0.30 in the marbles with prevailing assemblage of Bt + Ms + Cal + Qtz and rarely Tr + Cal + Qtz, locally also K-feldspar and albite are present. Mineral assemblages with grossular, vesuvianite and clinozoisite were rarely encountered in rocks richer in silicates. Such an assemblage is stable only at extremely high activity of  $H_2O$  (X<sub>CO2</sub> around 0.04).

#### (2) Vranov-Olešnice Unit and Velké Vrbno Unit

Marbles form large bodies (up to 50 m thick) in a complex of dominant muscovite-biotite metapelites (mica schists, gneisses) metamorphosed in amphibolite facies (garnet zone; kyanite-bearing metapelites also locally occur in the westernmost part, Sekanina 1965). Locally common intercalations of quartzites, minor metabasic rocks and graphite-rich rocks are closely associated with metacarbonates. Reliable data about mineral assemblages and metamorphic evolution of metapelites in these units are missing. Two distinct compositional types of marbles were recognised, calcite- and less abundant dolomite-dominated marbles, respectively (Sekanina 1965). The typical mineral assemblages Cal + Tr  $\pm$  Phl and Dol + Cal + Tr  $\pm$  Phl mostly exhibit Tr >> Phl, but locally Tr < Phl (Houzar et al. 2000a). The PTX conditions of metamorphism of these marbles were estimated from stability of the assemblages Tr + Cal + Qtz a Tr + Dol. and correspond to  $T_{max}$  = 580–620 °C at  $X_{CO2}$  = 0.2–0.7 and  $T_{min.}$  = 480–530 °C at  $X_{CO2}$  = 0.2–0.6 at  $P_{total}$  = 500 MPa (Houzar et al. 2000b).

#### (3) The Moldanubicum

The Moldanubicum is subdivided into three distinct units: the Gföhl Unit and the Monotonous and Varied units. The first unit is composed of high-grade metapelites, migmatites, amphibolites, granulites; lenticular bodies of mantle-derived garnet peridotite and pyroxenite commonly occur. Marbles and graphitic quartzite have been reported by Fuchs and Matura (1976). Sillimanite-garnetbiotite paragneisses and migmatites as well as marbles, calc-silicate rocks, quartzite, graphite-bearing rocks and amphibolite are common in the Varied Unit, cordierite migmatite occurs mainly in the Monotonous Unit. Metamorphic rocks of the Varied Unit experienced conditions in the range of 700–800 °C and 8–11 kbar. Later retrogression was characterized by 500–650 °C and 6 kbar (Petrakakis 1997).

Dolomite and calcite marbles from the Varied Unit of the Moldanubicum form bodies up to several tens of metres thick in sillimanite-garnet-biotite paragneisses and cordierite migmatites. They are associated with diopside gneisses, quartzites and amphibolites. In the surroundings of the Třebíč durbachite massif, dolomite-bearing rocks are common; in the western part, calcite marbles with a higher content of silicates and quartz occur together with quartzites (Houzar 1984, Novák 1989).

Metamorphic reactions and mineral assemblages in marbles in the eastern part of Moldanubicum were studied in detail (e.g., Novák 1989). Mineral assemblages of dolomite marbles, including phlogopite, forsterite, spinel, chlorite and clinohumite, correspond to the upper amphibolite facies. The older metamorphic assemblage M1, with phlogopite and tremolite, is typically overprinted by a younger HT/LP metamorphism M2 during which assemblages with spinel, forsterite and clinohumite originated mainly in the exocontact of the Třebíč durbachite massif. The estimated metamorphic conditions are  $T_{max} = 660 \text{ }^{\circ}\text{C}$ and P = 600 MPa for M1 event. Locally, retrograde mineral chlorite II and serpentine are abundant. Since reaction  $3 \text{ Tr} + 5 \text{ Cal} = 11 \text{ Di} + 2 \text{ Fo} + 5 \text{ CO}_2 + 3 \text{ H}_2\text{O}$  peak of the M2 metamorphism corresponds to P = 200 MPa, T = 620 °C and  $X_{CO2} < 0.3$  (Novák 1988, 1989, Houzar and Novák 1991, Novák and Houzar 1996). No older studies, however, show more frequent occurrence of assemblages with pargasitic amphibole and assemblages Spl + Dol, which may indicate a higher degree of metamorphism in marbles in the uppermost parts of the Varied Unit, which are immediately overlain by granulite complexes of the Gföhl Unit (Nová Ves u Oslavan, Kostníky u Jemnice). The minimum estimated values for metamorphism in the vicinity of Jemnice are max. 720 °C at 1 GPa (Kolenovská et al. 1997).

#### **Description of localities**

Localities typical for the respective units in their geological position and mineral assemblages were chosen to document changes in textures and CL of minerals in marbles with a gradually increasing grade of metamorphism from the middle greenschist facies to granulite facies (Fig. 1). Such localities were preferred, where new results of a detailed study of their mineral assemblages, together with chemical analyses of the minerals, are available (Houzar and Novák 1991, Novák and Houzar 1996, Houzar et al. 2000a).

#### Mineral reactions and CL observations

#### Lukov Unit

The studied marbles of the Lukov unit are grey-white to dark grey, fine- to medium-grained, locally with a high content of silicates and quartz, quartz and calcite segregations and late carbonate veins. The maximum PTX conditions of meta-morphism derived from the main assemblages Ms + Cal + Qtz and Rt + Cal + Qtz were approximately around P = 500 MPa, T < 450 °C and  $X_{CO2} < 0.2$  (compare Tracy and Frost 1991). Titanite as a product of reaction

$$Rt + Cal + Qtz = Ttn + CO_2$$
(1)

was only found near Čížov.

The CL study of calcite marble from Horní Dunajovice (biotite zone) revealed heteroblastic structure, mostly formed by angular grains of Fe-carbonates (prevailing Fe-calcite with FeO  $\geq$  1 wt.% and Fe-dolomite, rare ankerite, with dull brown or without CL). These grains are accompanied by recrystallized young (?) calcite (orange CL). Minor micas and rare tourmaline and rutile appear to be non-luminescent on CL. Quartz and probably albite exhibit blue and green CL, respectively, accessory apatite and REE-carbonates exhibit pale greenish yellow CL (Plate I, 1 and 2).

Calcite marble near Čížov (staurolite zone) consists of relatively homogeneous grains of calcite I with about 1 % FeO (brown CL). Small grains, intergranular filling and veins of calcite II with orange CL represent probably only the latest calcite as a product of retrograde metamorphism. Muscovite, biotite, rutile and sporadic tourmaline are non-luminescent minerals; quartz has blue CL and albite dark green CL (Plate I, 3 and 4).

Dominant simple textures in marbles of the Lukov Unit suggest that no metamorphic reactions between silicates and carbonates were found, or that no reactions took place during the formation of the mineral assemblage in the marble, which would produce new carbonates with different chemical composition. No younger metasomatic replacements, connected with a change in chemical composition of the rock were found (Houzar and Leichmann 2000). More complicated CL of carbonates in the marble from Horní Dunajovice is a result of non-homogeneous (mosaic) composition of particular carbonate grains. It is probably a

	1		
Locality	Unit	marble	mineral assemblage
<ol> <li>Horní Dunajovice, quarry in Křepička R. valley</li> </ol>	Lukov Unit	calcite	Cal + Qtz + Ms + Bt + Ank + Rt + Tur
2. Čížov near Znojmo, outcrops in the SW	Lukov Unit	calcite	$Cal + Qtz + Ms + Bt + Ab + Rt + Tur \pm Dol$
3. Jedov near Náměšt n/Osl. quarry in the SE	Olešnice Unit	calcite	Tr + Cal + Di + Tr + Ttn + Srp
4. Olešnice quarry near Lamberg	Olešnice Unit	calcite	$Tr + Cal + Qtz + Phl + Ttn \pm Dol \pm Py$
5. Jobova Lhota near Svojanov, outcrops, 500 m to the E	Olešnice Unit	calcite	$Tr + Cal + Phl + Qtz \pm Pl \pm Dol \pm Gr$
<ol> <li>Vranov near Znojmo, quarry in Junácké údolí valley</li> </ol>	Vranov Unit	dolomite	$Tr + Dol + Cal + Phl \pm Tlc$
7. Šléglov, outcrop about 1.5 km to the W	Velké Vrbno Unit	dolomite	$Tr + Dol + Cal \pm Phl$
8. Číchov, quarry near railroad	Moldanubicum (Varied Unit)	calcite	$Cal + Di + Kfs + Ttn + Qtz + Po \pm Tr \pm Pl \pm Bt$
9. Čechtín, outcrops in the SW	Moldanubicum (Varied Unit)	calcite	$Cal + Di + Kfs + Ttn + Po \pm Wo \pm Scp$
10. Krahulov near Třebíč, quarry 1 km to the N	Moldanubicum (Varied Unit)	dolomite	$Dol + Cal + Chu + Spl \pm Fo \pm Phl$
11. Moravské Budějovice Lukovská hora Hill	Moldanubicum (Varied Unit)	dolomite + calcite	a) Dol + Cal + Fo + Phl + Spl ± Prg b) Cal + Wo + Di + Ttn ± Scp
12. Kostníky, quarry near Želetavka R. valley	Moldanubicum (Varied Unit)	dolomite	$Dol + Cal + Srp + Fo + Phl + Po \pm Prg \pm Spl$
13. Nová Ves near Oslavany quarry in Oslava R. valley	Moldanubicum (Varied Unit)	dolomite	$Dol + Cal + Fo + Phl \pm Di \pm Srp \pm Spl$

Abbreviations of minerals after Kretz (1983)

relic texture, which was preserved due to a relatively weak metamorphism in the biotite zone. Mineral assemblages of the marbles of the Lukov Unit are then most likely a product of a simple coarsening and neocrystallization of calcite of sedimentary limestone with high quartz and phyllosilicate admixtures.

### Vranov-Olešnice Unit and Velké Vrbno Unit

Calcite (A) and dolomite (B) marbles were distinguished within these units:

(A) Typical calcite and calcite > dolomite marbles with grey tremolite porphyroblasts are known from Jobova Lhota and Olešnice. Calcite I (deep orange CL) as a product of coarsening prevails, but in association with tremolite and phlogopite (both non-luminescent) calcite II (pale orange CL) also occurs (Plate I, 5 and 6) as a product of reaction

$$5 \text{ Dol} + 8 \text{ Qtz} + \text{H}_2\text{O} = \text{Tr} + 3 \text{ Cal} + 7 \text{ CO}_2.$$
 (2)

This calcite contains relics of angular dolomite grains (brownish red CL) and quartz (blue CL). Accessory small albite grains (grey-green CL) associated with dolomite are typically present in some marbles from the Olešnice Unit (Sekanina 1965). The latest calcite III (pale yellow CL) commonly fills cracks of older grains of calcite and some silicates at all localities and originated during the latest metamorphic stage.

Slightly higher-grade metamorphosed calcite marbles close to the border with the Moldanubicum (Jedov near Náměšť nad Oslavou) have a typically unstable assemblage of Tr + Dol; the presence of diopside and maybe forsterite is also typical (Houzar and Novák 1991). Angular calcite I (deep orange CL) is overgrown by calcite II (yellow CL), which originated as a result of recrystallization of calcite I during brittle deformation of marble. Mineral assemblage is in disequilibrium, older tremolite (black) is overgrown or replaced by diopside (green CL). This reaction can be described by the equation

$$Tr + 3 Cal + 2 Qtz = 5 Di + 3 CO_2 + 2 H_2O.$$
 (3)

(B) In dolomite marbles, like near Vranov, diopside, phlogopite and tremolite are usually non-luminescent. Tremolite in equilibrium with dolomite (red CL) was found only near the locality of Šléglov (Velké Vrbno Unit). Tremolite from this locality shows a short-living blue CL (Plate II, 3). It is replaced by calcite with a distinct yellow luminescence. Apatite (pale yellow CL) in the form of very fine grains is an accessory. Dolomite marbles show usually a simple homeoblastic texture, consisting of homogeneous grains of dolomite I (red CL) and less common calcite I (orange CL). Indistinct zoning can be observed in larger calcite grains with lighter rims. No calcite was found at the contact of silicates (tremolite, phlogopite) with dolomite, so most likely reactions of tremolite origin, were:

$$2 \operatorname{Tlc} + 3 \operatorname{Cal} = \operatorname{Tr} + \operatorname{Dol} + \operatorname{CO}_2 + \operatorname{H}_2 \operatorname{O}$$
(4)

$$5 \text{ Tlc} + 6 \text{ Cal} + 4 \text{ Qtz} = 3 \text{ Tr} + 6 \text{ CO2} + 2 \text{ H}_2\text{O}.$$
 (5)

The problem of a reaction resulting in the formation of phlogopite cannot be clearly solved; it cannot be excluded that it originated by recrystallization of another phyllosilicate, which was contained in the original sedimentary (diagenetic) dolomite.

Marbles from the Olešnice Unit and Velké Vrbno Unit are good examples for the study of metamorphic reactions producing tremolite. Using transmitted light and CL, several mineral reactions producing early tremolite I (Tr I) were found (2), (4), (5) near Vranov, Olešnice, Šléglov and Velké Vrbno (Houzar et al. 2000c). Rare relics of dolomite and quartz found in large porphyroblasts of tremolite I in equilibrium with calcite II also indicate a participation of mineral reaction (2). Formation of calcite II is very likely always not related to reaction (2), but rather represents a recrystallization of calcite I. Both calcite I and tremolite underwent brittle deformation and their angular grains are rimmed and healed by younger calcite. Rare equilibrium assemblage Tr I + Dol suggests mineral reaction (4). The existence of reactions (4) and (5) is supported by the textural relations of early calcite I associated with relics of quartz and talc, and the reaction does not produce calcite II in equilibrium with tremolite (Houzar and Leichmann 2000, Houzar et al. 2000c).

#### Moldanubicum - Varied Unit

In the Varied Unit, calcite marbles (A) occur in sillimanite-biotite paragneisses in a sequence of rocks rich in quartzites SE of Jihlava. Calcite-dolomite marbles (B) are typical for HT/LP metamorphosed area west of the Třebíč durbachite massif. Relatively pure dolomite marbles (C) at localities immediately below the granulite complexes of the Gföhl Unit E of Mohelno (Nová Ves near Oslavany; Houzar and Novák 1991) or in the vicinity of Jemnice (Kostníky) are perhaps metamorphosed under conditions close to the granulite facies (Houzar 1999).

#### (A) Calcite marbles

Fine-grained calcite marbles (locality Číchov, U dráhy) are characterized by a mosaic texture of oriented calcite I (deep orange CL) and mineral assemblages produced by reaction (3) and reaction (6):

Tremolite and phlogopite do not show any CL effect. Very rare is a dark green short-living CL of diopside or retrograde tremolite after diopside in relatively Fe-enriched assemblage with pyrrhotite; quartz and K-feldspar show blue CL. The presence of K-feldspar might evidence reaction (6) or a similar reaction, which can produce K-feldspar in equilibrium with diopside. CL study revealed oscillatory zoning of K-feldspar (Plate I, 8), which indicates that it is not a product of this reaction, but was tectonically displaced from thin quartz-potassium feldspar dykes that are quite common at this locality.

Similar assemblages can be also found in calcite marbles in cordierite migmatites in exocontact of the Třebíč massif. Medium- to coarse-grained silicate-rich marbles, contain a relatively homogeneous calcite (orange CL), which represents probably a product of recrystallization with a complete rebuilding of older textures with quartz, tremolite and phlogopite during a younger HT/LP metamorphism. Acicular wollastonite (yellowish green CL) is locally replaced by retrograde calcite (yellow CL) while SiO<sub>2</sub> has to be removed (compare Kerrick et al. 1991). Wollastonite is accompanied by Fe-diopside (short-living deep green CL) in a mosaic of Mg-calcite (dark orange CL), e.g., in calcite marble at Lukov near Moravské Budějovice (Plate II, 4). Other marbles (e.g., Čechtín) contain common grains of diopside (no CL), Kfs (blue CL), titanite (no CL) and relics of biotite (no CL). Hypautomorphic grains of scapolite (meionite) showing a typical green to yellow-green short-living CL (Plate II, 5) were produced by the reaction:

$$Cal + 3 Pl = Scp.$$
(7)

#### (B) Calcite-dolomite marbles

Occurrences of dolomite marbles with spinel and clinohumite are typical in exocontact of the Třebíč massif (Novák and Houzar 1996). Clinohumite does not show any CL and occurs in assemblage with dolomite (red CL), fine-grained calcite I (bright orange CL), forsterite, chlorite, spinel and metamorphic Mg-calcite II (orange CL). Small exsolutions of dolomite are common in metamorphic calcite (compare Kretz 1988). Such features have not been formerly reported from the Moldanubicum (Novák 1988, Novák and Houzar 1996) but we found such exsolution e.g. in the marble from Krahulov (Plate II, 1 and 2). The exsolutions locally have a calcite "halo" with a brighter CL. Mg-spinel (green CL), clinohumite and forsterite (no CL) were also described in this assemblage. Relict character of dolomite and common Mg-calcite II evidence these reactions:

$$4 \operatorname{Fo} + \operatorname{Dol} + \operatorname{H}_2 O = \operatorname{Chu} + \operatorname{Cal} + \operatorname{CO}_2$$
(8)

and possibly

$$4 \text{ Chl} + 11 \text{ Dol} = 3 \text{ Chu} + 4 \text{ Spl} + 11 \text{ Cal} + 13 \text{ H}_2\text{O} + 11 \text{ CO}_2$$
(9)

and reactions involving phlogopite: Phl + Dol  $\rightarrow$  Fo + Spl + Cal + Chu + K<sub>2</sub>O + CO<sub>2</sub> + H<sub>2</sub>O (Novák 1988, 1989).

CL study of calcite-dolomite marbles from Moravské Budějovice (Lukovská hora Hill) disclosed grains of dolomite (brownish red CL) and calcite I (deep orange CL), with lath-shaped Phl (black), containing commonly spinel (green CL) and forsterite with rims of calcite II (orange CL), locally also diopside and pargasitic amphibole (black or dark green). This assemblage also contains calcite II (pale orange CL), which is a product of metamorphic reactions. Although relics of tremolite were not preserved, it is possible to assume from a common equilibrium assemblage Fo+Cal  $\pm$  Spl that, for example, the reaction

$$Tr + 11 Dol = 8 Fo + 13 Cal + 9 CO_2 + H_2O$$
(10)

described from the Moldanubicum by Novák (1989) took place here as well. Spinel can sometimes show zoning, in which Mg-spinels including Fe-rich rims of larger grains show a light green CL (Plate II, 6). Assemblage Dol + Spl, yet unknown from the Moldanubicum, shows a possibility of the presence of other reactions, since the occurrence of spinel without calcite is most likely a product of a reaction of chlorite and calcite. When dolomite, diopside, forsterite or Al-amphibole originate, such reaction demands conditions of P = 500 MPa, T > 600 °C and a high  $X_{CO2}$  (Bucher-Nurminen 1981); at low  $Xco_2$ , assumed in this region by Novák and Houzar (1996), T would exceed 800 °C. Pargasite and/or diopside (both without CL) were found in the marbles of Lukovská hora Hill, however, their position is rather relict and reminds of a possible presence of the reaction

Al-Amf + 11 Dol = 7 Fo + Spl + 13 Cal + 9 CO<sub>2</sub> + 
$$H_2O$$
 (11)

described, e.g., by Kretz (1980). Spinel in dolomite could also be a result of a breakdown of unknown Al-silicate without any reaction with carbonate, connected with  $SiO_2$  migration without a possibility of determination of a particular reaction.

#### (C) Dolomite marbles

These marbles are characterized by red CL of dolomite (orange red to dark red CL). Spinel grains (green CL) are usually embedded in dolomite. Calcite I (orange CL) is uncommon and silicates are missing in association with it. Calcite II associated with non-luminescent forsterite is usually very inhomogeneous (orange CL), which is likely a result of variations in Mg (-Fe) contents within one grain. Marble with a homeoblastic texture of dolomite (red CL), including forsterite (black) with rims of diopside (bluish white CL) represents another type (Plate II, 7). They are probably products of the reaction:

$$2 \text{ Fo} + 4 \text{ Cal} + 2 \text{ CO}_2 = \text{Di} + 3 \text{ Dol}$$
 (12)

typical for granulite facies with high  $X_{CO2}$  (Bucher-Nurminen 1981, Sauter 1983). Forsterite is frequently entirely altered into serpentine (black) with "vein" dolomite (deep red CL) in intergranular space. This might be a product of the reaction:

$$34 \text{ Fo} + 20 \text{ Cal} + 31 \text{ H}_2\text{O} + 20 \text{ CO}_2 = \text{Srp} + 20 \text{ Dol.}$$
(13)

Calcite I (deep orange CL) is generally rarer in this rock. Elsewhere, the assemblage of forsterite + calcite II (orange) with relics of dolomite (brown) is a product of reaction (10). Relics of tremolite document such an assemblage near Kostníky. The overall texture of marble is, however, more complicated, as shown by the assemblages of forsterite with spinel (green CL) and relics of older pargasitic amphibole (green CL). Some dolomite grains are also distinctly zoned (light cores, dark rims, sometimes one lighter zone in the outermost part of the grain, Plate II, 8). Close to these dolomite grains, forsterite is completely serpentinized and therefore a modified reaction

$$34 \text{ Fo} + 31 \text{ H}_2\text{O} + 20 \text{ CO}_2 = \text{Srp} + 20 \text{ Mag}$$
 (14)

(Trommsdorf and Evans 1977) can be assumed. If the "classic" reaction

$$5 \text{ Fo} + \text{H}_2\text{O} = 2 \text{ Srp} + \text{SiO}_2 + 4 \text{ MgO}$$
 (15)

was to take place, SiO<sub>2</sub> should have been removed.

#### **Conclusions and summary**

The behaviour of siliceous calcite marbles with low content of Fe, Mg-richer carbonates in transition from the biotite to staurolite zones was documented in the Lukov Unit of the Moravicum. The main observed difference is the gradual homogenisation of the original sedimentary texture, which is visible mainly in Fe, Mg-carbonate grains, whereas no metamorphic reactions between them and silicates took place. The Fe-bearing calcite, Fe-dolomite and ankerite show CL in brown hues. It is interesting that inhomogeneity of grains is observed in CL, contrary to their homogeneity in TrL (Horní Dunajovice, biotite zone). Marbles from Čížov (staurolite zone) consist mainly of calcite, which includes unsharp relics of Fe-bearing calcite (FeO ~ 1 %). Similar changes in CL during homogenisation of carbonate grains are known from some marbles in contact aureoles (Schmid and Ramseyer 1996).

Reactions involving tremolite in siliceous dolomite and calcite marbles, formed in amphibolite facies from the Vranov-Olešnice and Velké Vrbno units, were documented (Jobova Lhota, Olešnice-Lamberk). Tremolite commonly shows no CL, but it has often a short-living blue CL in pure dolomite marbles (e.g., Šléglov). Based on the CL study, it was possible to distinguish several equilibrium associations with tremolite and several generations of carbonates. Dolomite grains are usually not zoned, showing red CL, and occurring mostly as relics in some assemblages. A part of calcite is a product of coarsening of the original sedimentary carbonate (Cal I), whereas the other part is a result of metamorphic reactions (Cal II). The youngest calcite III (bright yellow CL) partly occurs. Its origin is probably connected to changes of marbles at LT/LP retrograde stage. This calcite III reminds hydrothermal carbonates in its zoning. Mineral assemblages and CL of the individual minerals resemble those in marbles of the Connemara region, Ireland (Yardley and Lloyd 1989).

In the Varied Group of the Moldanubicum, tremolite, phlogopite and titanite of calcite marble do not show any CL effect with very minor exceptions. Very rare is a dark green short-living CL of diopside or retrograde Fe-tremolite after diopside. Calcic scapolite (meionite) showing a typical green to yellow-green short-living CL and wollastonite observed in CL may be locally replaced by retrograde calcite (yellow CL), while SiO<sub>2</sub> has been removed.

Mineral reactions in dolomite marbles of higher amphibolite to granulite facies were studied, with assemblages including forsterite, diopside, spinel and pargasitic amphibole. Dolomite grains show quite uniform red CL but several generations of dolomite in marbles were confirmed even within a single thin section. The oldest grains of dolomite I are homogeneous or zoned with darker dolomite II on grain rims. They are probably a result of coarsening of sedimentary (diagenetic) dolomite. Dolomite III forms tiny exsolutions of dolomite in Mg-calcite (Plate II, 2). Dolomite IV (usually red-brown CL) is present in serpentine marbles, where serpentine replaced forsterite or other Mg-silicates. Dolomite IV together with magnesite might present products of retrograde phases of metamorphism (Plate II, 7). CL of common silicates is quite different in calcite marbles and dolomite marbles. This might be connected with an overall higher amount of Fe in calcite marbles (Houzar, unpublished data). Silicates and some spinels from dolomite marbles are usually close to the Mg end-member (e.g., Kretz 1980, Novák 1986, 1989).

The present paper gives some examples of how CL can be used for the study of mineral assemblages and reactions in marbles, metamorphosed in the range from greenschist to granulite facies. CL enables to study the products of particular mineral reactions in carbonate rocks and to contribute to the determination of equilibrium assemblages, which would be suitable for the evaluation of the PTX conditions of their origin. This method is a good supplement to a common TrL microscopy. CL can also be utilised in comparative studies of experimental and theoretical reactions with the situation in nature, where some significant differences can be found (Kerrick et al. 1991). It can also be useful during stable isotope studies of marbles (Yardley and Lloyd 1989).

Acknowledgements. This work was partially sponsored by the Grant Agency of the Academy of Sciences CR A3408902/1999 and MKOCEZ00F2402 for SH. The author wishes to thank M. Novák for his discussion and P. Korbel for the translation of the manuscript, as well as B. Kříbek and M. Pagel for critical reviews.

#### References

- Batík P. (1984): Geologická stavba moravika mezi bítešskou rulou a dyjským masívem. Věst. Ústř. úst. geol. 59, 6, 321–330.
- Bernroider M. (1989): Zur Petrogenese präkambrischer Metasedimente und cadomischer Magmatite im Moravikum. Jb. Geol. Bundesanst. 132, 349–373.
- Bucher-Nurminen K. (1981): Petrology of chlorite-spinel marbles from NW Spitsbergen (Svalbard). Lithos 14, 203–213.
- Fuchs G., Matura A. (1976): Zur geologie des Kristallines der südlichen Böhmischen Masse. Jb. Geol. Bundesanst 119, 1–43.
- Gross Ch. J., Weber K., Vollbrecht A., Siegesmund S. (1999): Cathodoluminescence and electron microprobe study of dolomitic marbles from Namibia: Evidence for hydrothermal alteration. Z. Dtsch. geol. Gesell. 150, 2, 333–357.
- Haberman D., Neuser R. D., Richter D. K. (1996): Low limit of  $Mn^{2+}$  activated cathodoluminescence of calcite: state of the art. Sed. Geol. 116, 13–24.
- Haberman D., Neuser R. D., Richter D. K. (2000): Quantitative High Resolution Spectral Analysis of Mn<sup>2+</sup> in Sedimentary Calcite. In: Pagel M., Barbin V., Blanc P., Ohnenstetter D. (eds) Cathodoluminiscence in Geosciences. Springer, Berlin, pp. 136–145.
- Höck V. (1975): Mineralzonen in Metapeliten und Metapsamiten der Moravischen Zone in Niederösterreich. Mitt. Geol. Gesell. (Wien) 66–67, 49–60.

- Höck V. (1995): Moravian zone: Metamorphic evolution. In: Dallmeyer R. D., Franke W., Weber K. (eds) Pre-Permian Geology of Central and Eastern Europe. Springer-Verlag, Berlin, pp. 541–553.
- Höck V., Marschallinger R., Topa D. (1991): Granat-Biotit-Geothermometrie in Metapeliten der Moravischen Zone in Österreich. Österr. Beitr. Meteor. Geophys., H 3, 149–167.
- Houzar S. (1984): Lokality mramorů a erlanů v moravském moldanubiku. Přírod. Sbor. Západomorav. Muz v Třebíči 13, 9–23.
- Houzar S. (1999): Charakteristika mramorů u Jemnice na jz. Moravě. Geol. Výzk. Mor. a Slez. v R. 1998, 6, 112–114.
- Houzar S., Leichmann J. (2000): Application of cathodoluminescence microscopy to the study of metamorphic reactions in marbles; examples from Moravian Zone. Acta Miner. Petrogr. Univ. Szeged 41, 53.
- Houzar S., Novák M. (1991): Dolomite marbles at contact of the Moldanubicum and Moravicum in the area between Jasenice and Oslavany. Acta Mus. Morav. Sci. nat. 76, 83–94.
- Houzar S., Novák M., Němečková M. (2000a): Distribuce tremolitových mramorů v Českém masivu. Acta Mus. Morav., Sci. geol. 85, 105–123.
- Houzar S., Němečková M., Novák, M. (2000b): Zpráva o výzkumu mramorů u Kuroslep na západní Moravě (olešnická skupina). Geol. Výzk. Mor. a Slez. v R. 1999, 77, 120–122.
- Houzar S., Novák, M., Němečková M., Leichmann J. (2000c): Geological distribution of tremolite marbles in the Bohemian Massif and CL-study of their prograde metamorphic reactions in the Olešnice Group. Geolines, Abstracts Conf. Czech Tectonic Group, Bublava, 10, 31–32.
- Kerrick D. M., Lasaga A. C., Raeburn S. P. (1991): Kinetics of heterogeneous reactions. In: Kerrick D. D. (ed.) Contact metamorphism, Reviews in Mineralogy 26, Mineral. Soc. Amer. 26, pp. 583–671.
- Kolenovská E., Schulmann K., Klápová H., Štípská P. (1997): Teplotně tlakové podmínky metamorfózy hornin v okolí Jemnice na jižní Moravě. Sbor. II. semináře Čes. tektonické skup. Ostrava 1997, 40–41.
- Konopásek J., Schulmann K., Johan V. (2002): Eclogite-facies metamorphism at the eastern margin of the Bohemian Massif – subduction prior to continental underthrusting?. Eur. J. Mineral. 14, 701–713.
- Kretz R. (1980): Occurrence, mineral chemistry and metamorphism of Precambrian carbonate rocks in a portion of the Grenville Province. J. Petrology 21, 573–620.
- Kretz R. (1983): Symbols for rock-forming minerals. Amer. Mineralogist 68, 277–279.
- Kretz R. (1988): SEM study of dolomite microcrystals in Grenville marble. Amer. Mineralogist 73, 619–631.
- Machel H. G. (2000): Application of cathodoluminescence to carbonate diagenesis. In: Pagel M., Barbin V., Blanc P., Ohnenstetter D. (eds) Cathodoluminiscence in Geosciences. Springer Verlag, Berlin, pp. 160–166.
- Marshall D. J. (1988): Cathodoluminescence of geological materials. Unwin Hyman, Boston.
- Mísař Z. (1995): Moravosilesian Zone. VIII.C.1 Stratigraphy. In.: Dallmeyer R. D. et al. (eds) Pre-Permian geology of Central and Eastern Europe. Springer-Verlag, pp. 522–529.
- Novák M. (1986): Minerální reakce v dolomitických mramorech. Report, Fac. Sci. Charles Univ. Praha.
- Novák M. (1988): Petrologie metamorfovaných dolomitických hornin při severovýchodním okraji moldanubika. Report, PhD Thesis, Fac. Sci. Charles Univ. Praha.
- Novák M. (1989): Metamorfóza dolomitických hornin při severovýchodním okraji moldanubika. Acta Mus. Morav., Sci. nat. 74, 7–51.
- Novák M., Houzar S. (1996): The HT/LP metamorphism of dolomite marbles in the eastern part of the Moldanubicum; a manifestation of heat flow related to the Třebíč Durbachite Massif. J. Czech Geol. Soc. 41, 3–4, 139–146.
- Petrakakis K. (1997): Evolution of Moldanubian rocks in Austria: review and synthesis. J. metamorphic Geol. 15, 203–222.
- Pivnička L. (1995): Metamorfóza lukovské skupiny moravika dyjské klenby. Report, Diploma Thesis. Fac. Sci. Masaryk Univ. Brno.
- Sauter P. C. C. (1983): Metamorphism of siliceous dolomites in the high-grade. – Precambrian of Rogaland, SW Norway. Geologica Ultraiect. 32, 1–143.
- Sekanina J. (1965): Minerály a jejich genetické vztahy k horninám na území geologické mapy 1 : 50 000, list M 33-93-B (Bystřice nad Pernštejnem). Report, Min.-petr. Dpt., Moravian Museum, Brno.

- Schmid J., Ramseyer K. (1996): Effect of static recrystallization of calcite on its cathodomicrofacies. Int. Conf. on Cathodoluminescence and related techniques in Geosciences and geomaterials Nancy.
- Tracy R. J., Frost B. R. (1991): Phase equilibria and thermobarometry of calcareous, ultramafic and mafic rocks, and iron formations. In: Kerrick M. D. (ed.) Contact metamorphism. Reviews in Mineralogy, 26, Mineral. Soc. Amer., pp. 207–289.
- Trommsdorff V. V., Evans, B. W. (1977): Antigorite-ophicarbonates: phase relations in a portion of the system CaO-MgO-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub>. Contr. Mineral. Petrology 60, 39–56.
- Yardley B. W. D., Lloyd G. E. (1989): An application of cathodoluminescence microscopy to the study of textures and reactions in high-grade marbles from Connemara, Ireland. Geol. Mag. 126, 4, 333–337.

Handling editor: Jan Pašava

 $\rightarrow$ 

 $\rightarrow \rightarrow$ 

Plate I

1 – Marble rich in biotite and muscovite with albite and quartz. Horní Dunajovice, Lukov Unit, Moravicum. Crossed polars, transmitted light = TrL. The width of view of all photomicrograph is 5 mm.

2 – CL image of marble from Horní Dunajovice.

A mosaic of inhomogeneous grains of Fe-bearing carbonates (Fe-calcite, Fe-dolomite, ankerite) with dull brown CL, calcite (orange) and phyllosilicates (non-luminescent).

3 - Calcite marble composed of isometric calcite, elongated biotite and muscovite, and accessory albite and quartz. Čížov near Znojmo, Lukov Unit, Moravicum. Crossed polars, TrL.

4 – CL image of marble from Čížov.

Large grains of calcite I with brownish red CL rimmed by calcite II (orange), quartz (blue), albite (greyish green) and biotite and muscovite (both non-luminescent).

5 – Tremolite-bearing dolomite-calcite marble with phlogopite and plagioclase. Jobova Lhota, Olešnice Unit, Moravicum. Crossed polars, TrL. 6 – CL image of identical marble from Jobova Lhota.

Xenomorphic dolomite grains (brownish red), black tremolite-magnesiohornblende porphyroblasts and grains of calcite I (dark orange) are healed calcite II (orange). Elongated phlogopite (black) and small grain of oligoclase (grey) and zircon (whitish blue) are present as minor minerals.

7 - Silicate-rich calcite marble from Číchov - "U dráhy". Varied Unit, Moldanubicum. Crossed polars, TrL.

8 - CL image of an identical marble from Číchov.

Zoned blue (dark to pale CL) K-feldspar, diopside (short-lived green CL) and quartz (black) with xenomorphic grains of calcite I (pale brown-red CL) is healed calcite II (orange).

#### Plate II

1 - Grain of calcite with exsolutions of dolomite, clinohumite and forsterite. Krahulov, Varied Unit, Moldanubicum. Crossed polars, TrL.

2 - Microstructures visible by CL in the dolomite marble – a large grain of calcite (orange red) with exsolutions of dolomite (red), clinohumite and forsterite (non luminescent).

3 – Tremolite-bearing dolomite marble from Šléglov (Velké Vrbno Unit, Silesicum), CL microphotograph illustrating short-lived blue CL of pure tremolite in dolomite matrix (red) and minor calcite (orange).

4 – Wollastonite-calcite marble from Moravské Budějovice – Lukovská hora Hill (Varied Unit, Moldanubicum), CL images. Wollastonite (yellowish green) is replaced by young calcite (yellow), non-luminescent diopside, in calcite (orange) matrix.

5 – Silicate-rich scapolite-bearing calcite marble from Čechtín (Varied Unit, Moldanubicum), CL images. Mejonite grain (green) with carbonated centre (green-yellow calcite III) is major mineral in calcite marble with accessories: quartz (blue CL), K-feldspar, diopside, titanite and phlogopite (all black, CL-out).

6 – Calcite-dolomite marble with forsterite, phlogopite and spinel. Varied Unit, M. Budějovice – Lukovská hora Hill, Moldanubicum. CL images. Angular dolomite (red) with small isometric spinel grains (green) in calcite (orange) and isometric forsterite and elongated phlogopite and pargasite grains. All silicates have no CL, only pargasitic amphibole may be sometimes green in CL.

8 – Dolomite marble with forsterite, phlogopite and pyrrhotite. Unusual Fe-bearing assemblage of dolomite marble. Varied Unit, Kostníky near Jemnice, Moldanubicum. CL images. Zoned grains of dolomite (dark red – pale red) and calcite II (orange) as a product of reactions with serpentinized forsterite and phlogopite (both black).

<sup>7</sup> – Dolomite marble with serpentine and diopside. Varied Group, Nová Ves near Oslavany, Moldanubicum. CL images. Serpentinized grains of forsterite (black) are rimmed by pure Mg-diopside (bluish white) in dolomite matrix composed of inhomogeneous grains of dolomite (red – dark red CL).



















1















Plate II