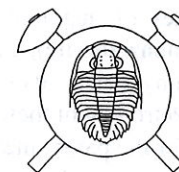


Formation conditions of various calcite types and unusual alteration products of wollastonite in calcite marble near Nezdice (Varied Group of Moldanubicum), Czech Republic



Podmínky vzniku různých typů kalcitu a pseudomorfóz po wollastonitu v kalcitickém mramoru u Nezdic (pestrá skupina moldanubika) (Czech summary)

(3 text-figs., 1 plate)

KAREL ŽÁK - PETR DOBEŠ - STANISLAV VRÁNA

Czech Geological Survey, Klárov 3, 118 21 Praha 1, Czech Republic

Extensive calcite-rich replacements after wollastonite have been found in an abandoned marble quarry near Nezdice, Šumava Mts., southern Czech Republic. Because any natural reversals of wollastonite reaction both in high-temperature and low-temperature environment are rare, combined mineralogical and stable isotope study of these pseudomorphs was performed. Other types of calcite observed in the quarry include marble in the zones of metamorphic decarbonation, hydrothermal vein calcite and calcite related to karstification process. Stable isotope and fluid inclusion methods were used to study the other types of calcite for comparison purposes.

A plausible scenario of the formation of the calcite pseudomorphs involves the following two step evolution mode:

(1) transformation of wollastonite to optically and X-ray amorphous phase (which could probably result from a high-rate tectonic deformation or shock wave compression), (2) reaction of the relatively unstable amorphous phase with water having high contents of CO_2 to CaCO_3 , mainly in the zone of supergene alteration. Formation of the secondary carbonates during weathering is strongly indicated by oxygen and carbon isotope composition. The carbonate-rich pseudomorphs after wollastonite still contain relics of the optically and X-ray amorphous phase which formed by transformation of wollastonite and retains its acicular crystal shape.

Alternative modes of formation of the pseudomorphs, including, e.g., a spontaneous decomposition of wollastonite to $\text{CaO} + \text{SiO}_2$ (due to shock wave deformation) during the step (1) or high-temperature reaction of a part of wollastonite with calcite (from the enclosing marble) to larnite, spurrite, or other very high-temperature minerals (also an alternative of step 1) could not be supported by observation; no remains of CaO or larnite were observed. Such unstable high-temperature minerals formed from wollastonite would transform to CaCO_3 -rich pseudomorphs on exposure to water having a high content of CO_2 .

Formation of the pseudomorphs by incongruent dissolution of wollastonite in the zone of weathering is not supported by observation - wollastonite behaviour as a stable mineral during weathering is well known. Associated diopside, quartz, and primary calcite show no replacement by secondary calcite. Stable isotope analyses and fluid inclusion study of calcite crystals coating some open fractures in the marble quarry indicate that this hydrothermal activity has no connection with formation of the pseudomorphs after wollastonite.

Key words: wollastonite, calcite-rich pseudomorphs after wollastonite, oxygen and carbon isotopes in calcite, fluid inclusions, deformation of marble, Moldanubian Zone

Introduction

Many different types of calcite that formed by a wide variety of processes occur in marble bodies in an abandoned quarry near Nezdice, Šumava Mts., southern Czech Republic. The marble bodies are located near Nezdice, Ostružno and Strašín, embedded in a complex of sillimanite-cordierite-biotite gneisses and migmatites located in the southern part of the Sušice Varied Unit. The Sušice Varied Unit is a part of the Varied Group of the Moldanubian rocks of amphibolite facies grade metamorphism. The impure marble bodies were influenced by metamorphic decarbonation reactions involving carbonate minerals, silicate minerals and metamorphic fluids. Other decarbonation reactions probably occurred along the contacts of the marble boudin with augite microgranodiorite dyke which is partly amygdaloidal. Based on paleomagnetic studies of the dyke (Krs - Vrána 1994), a Lower Permian age was determined for intrusion of the augite microgranodiorite. The Nezdice quarry contains hydrothermally altered zones and a variety of hydrothermal calcite veins that fill open fractures. The youngest generation of calcite was formed as a result of weathering of the marble.

Among various types of calcite present in the marble, an unusual fine-grained, extensive calcite-rich replacement of wollastonite attracted our attention. Initial X-ray diffraction studies indicated that aragonite was also present in the poly-mineral replacements of wollastonite. In the Moldanubian marbles and contact skarns, alteration of wollastonite has not been previously reported. Harley and Santosh (1995) described natural inversion of the wollastonite reaction under granulite facies conditions, resulting in approximately stoichiometric aggregate of calcite and quartz replacing wollastonite. To investigate the extensive and spontaneous transformation of wollastonite to calcite-rich pseudomorphs, combined mineralogical, stable isotope and fluid inclusion study of various carbonate types present in the Nezdice quarry was undertaken.

Local geology and studied samples

The marble bodies near Nezdice, Ostružno and Strašín are embedded in a complex of sillimanite-cordierite-biotite gneisses and migmatites. The peak metamorphic conditions of the last Variscan high-temperature, low-pressure metamorphism were estimated at 600-650 °C and 480-540 MPa by Pertoldová (1993) and Lellák (1993). Minor dy-

kes of augite microgranodiorite (transitional to quartz monzodiorite), in part with calcite-chlorite-quartz filled amygdales, also occur in the surrounding of Nezdice. Petrology of these dykes indicates extra high temperatures for the parent melt; one of the dykes is exposed 30 m higher in the slope above the Nezdice quarry.

During the retrograde phases of regional metamorphism, emplacement of granite bodies, and a quick uplift of this unit, several periods of intensive hydrothermal circulation occurred in the region surrounding the study area. An abandoned mining district of mesothermal gold-bearing quartz veins was exploited in the past and is prospected recently close to town of Kašperské Hory, located several km south of the study area. Ore veins are arranged here along a regional E-W trending shear zone and are characterised by minor carbonate deposition during the younger development phases. In the Nezdice quarry itself, the marbles are hydrothermally altered on a local scale and calcite fills open tensional fractures of N-S direction.

The youngest phase of geological development is related to weathering processes. The marbles are locally influenced by karstification, dissolution of carbonates, and deposition of newly formed calcite of karstic type (flowstone films). An unusual type of alteration and weathering products is represented by the above mentioned CaCO_3 -rich pseudomorphs after wollastonite-rich bands in marble, along a tectonically disturbed zone in the central part of the quarry. The wollastonite layers in calcite marble are up to 4 cm thick, the alteration is often incomplete. To investigate the origin of the calcite-rich pseudomorphs, various carbonate types present in the Nezdice quarry and at nearby localities were studied (Table 4).

Mineralogical and X-ray diffraction study of the pseudomorphs after wollastonite

The nearly monomineral wollastonite layers in marble consist of radiating aggregates of wollastonite up to 5 cm long. The front of alteration transgressed across the radiating aggregates and the original radiating and fibrous pattern is retained by the pseudomorphs which have a chalk-like appearance. The wollastonite-rich horizon with alteration phenomena is exposed over an area $> 10 \text{ m}^2$. Wollastonite replacement is also observed in thin sections on microscopic scale. Alteration is often extensive where wollastonite formed nearly monomineral aggregates. Distal protrusions and isolated wollastonite crystals enclosed in primary calcite often remain unaltered. It is suggested that this pattern of wollastonite transformation or preservation may reflect differences in plastic deformation properties between calcite and wollastonite. In calcite-rich domains deformation would be accommodated dominantly by calcite.

The pseudomorphs are bound by the frame of the former wollastonite-primary calcite interfaces, i.e., interfaces between primary calcite and the pseudomorph aggregate are common. Microscopic and SEM observations show that individual crystals comprising the pseudomorphs are

less than 1 μm in diameter. Two hand-picked samples (samples SNZ 1, and SN 44, Table 1) of the pseudomorphs were used for X-ray mineral identification. Sample SNZ 1 shows little evidence of weathering. However, minor porosity in sample SN 44 suggests that weathering has affected this sample. For both samples an untreated sample and insoluble residue after leaching in 9% HCl were studied by X-ray diffraction (Table 1). Because of the nature of the samples, a small amount of marble matrix around the pseudomorphs, estimated to $< 20 \text{ wt. } \%$, was also present in the selected material. This matrix component contributes calcite, diopside and quartz to the sample analyzed (Tables 1 and 3).

Table 1. X-ray identification of phases in the pseudomorphs

Sample No.	Untreated sample	Residue after leaching in 9% HCl
SN 44	calcite	diopside
	quartz	quartz
	aragonite	
	diopside	
SNZ 1	calcite	wollastonite
	quartz	quartz
	wollastonite	diopside
	diopside	

The X-ray measurements were conducted using the diffractograph Dron 3, Cu/Ni radiation at 35 kV, 20 mA, in the range 4.00 to 74.00 $^{\circ}2\theta$, step 0.05 $^{\circ}2\theta$

Mineral compositions in wollastonite marble containing the pseudomorphs were studied by microprobe analysis (Table 2). The pseudomorphs produce poor quality, uneven surface which affects quality of measurements. Several compositions measured on the pseudomorphs are plotted in Fig. 1 after recalculation to 100%. One sample of the pseudomorphs, No. SNZ 1, 2 g in weight, was used for wet analyses (Table 3).

Optical microscopy of the insoluble residue from sample SN 44 in grain mounts using immersion liquids shows the presence, besides diopside and quartz, of abundant isotropic fibres, which represent alteration product of former wollastonite. The fibres have brownish-grey colour and exhibit irregular non-planar features running approximately across the fibres. Due to the small width of the fibres, their composition remains unknown. X-ray measurements (Table 1) indicate that this material is probably amorphous. In sample SNZ 1 the insoluble pseudomorphs are present besides fresh wollastonite (Pl. Id).

These observations show that the optically isotropic pseudomorphs after wollastonite seen in thin sections are composed of two types of material, which are not resolved by optical microscopy: (1) very fine-grained ($< 1 \mu\text{m}$) aggregates rich in calcite (+ some SiO_2), which appear isotropic because of the small grain size and (2) isotropic and probably X-ray amorphous pseudomorphs after wollastonite, which retain approximately the shape of former wollastonite crystals (Pl. Id) and which are insoluble in 9% HCl.

The composition of the pseudomorphs indicated by wet analysis (Table 3) and a relatively more homogeneous group of compositions calculated from the microprobe

Table 2. Electron microprobe analyses of minerals in wollastonite marble; sample SN 44

Mineral	Diopside (n = 9)	Wollastonite (n = 3)	Calcite (n = 2)
SiO ₂	55.45	51.35	0.12
TiO ₂	0.03	0.00	0.00
Al ₂ O ₃	0.22	0.08	0.05
FeO	0.52	0.04	0.00
MnO	0.02	0.00	0.05
MgO	17.79	0.11	0.06
CaO	26.06	48.10	55.83
Na ₂ O	0.17	0.05	0.12
K ₂ O	0.02	0.01	0.00
CO ₂	n.d.	n.d.	43.77*
Total	100.28	99.74	100.00*
Number of cations	(O=6)	(O=3)	(O=6)
Si	2.010	0.995	0.033
Al	0.010	0.002	0.002
Cr	0.001	0.002	0.000
Ti	0.001	0.000	0.000
Fe	0.016	0.001	0.000
Mn	0.001	0.000	0.001
Mg	0.956	0.003	0.003
Ca	1.006	0.999	1.979
Na	0.012	0.002	0.008
K	0.001	0.000	0.000
C	-	-	1.972

* - CO₂ calculated to 100 % of analysis

All iron calculated as FeO

Table 3. Wet chemical analysis of pseudomorphs after wollastonite

SiO ₂	24.11	Na ₂ O	0.03	Calculated mineralogical composition, wt. %	
TiO ₂	<0.005	K ₂ O	0.04		
Al ₂ O ₃	0.34	P ₂ O ₅	0.07		
Fe ₂ O ₃ ^t	0.08	CO ₂	28.82	CaCO ₃	65.4
MnO	0.015	LOI*	0.53	SiO ₂	16.1
MgO	1.59	H ₂ O ⁻	0.46	diopside	8.6
CaO	41.84	Total	98.20	wollastonite	6.2

LOI* loss on ignition, value after subtraction of CO₂ and H₂O⁻

The analysis was made in the Chemical Laboratory of the Czech Geological Survey, Prague; Analyst: J. Šikl

analyses are plotted in Fig. 1. The compositions are shifted from the wollastonite-calcite join towards the SiO₂ apex, in agreement with the presence of quartz and diopside originating from the marble matrix around the pseudomorphs. The composition of the pseudomorphs is dominated by CaCO₃ which implies a significant CaCO₃ metasomatism and desilication of the wollastonite sites. As seen in Fig. 1, composition of the pseudomorphs also can derive from carbonation of one of the very high-temperature minerals arising by reaction of wollastonite with calcite, i.e., larnite, hatrurite, spurrite or tilleyite. We have found no evidence for a former presence of these minerals.

Deformations observed in thin sections are of interest for the mode of formation of amorphous pseudomorphs after wollastonite. Several examples of deformation textures are documented in Pl. I, which also shows relations of pseudomorphs after wollastonite to preserved wollastonite. In summary, deformations observed include mosaicism in wollastonite, deformation twinning in diopside (Pl. Ie) and titanite, birefringence fringes in diopside (Pl. If), kink-

bands in phlogopite, local brittle disintegration of calcite in subgrain mosaic, plastic deformation of calcite including rotation of cleavage planes by angles of up to 40°, and a strong undulous extinction in quartz. The absence of planar deformation features in quartz indicates that dynamic compression was <5 GPa.

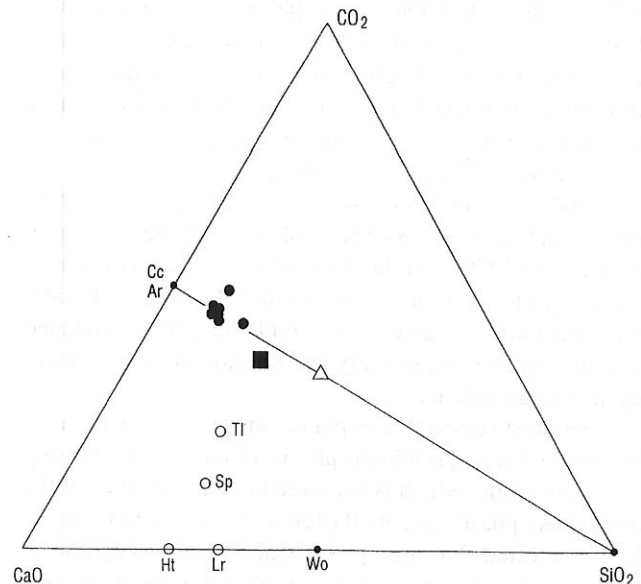


Fig. 1. Composition of pseudomorphs after wollastonite plotted in CaO-SiO₂-CO₂ triangle. Phases actually present: Cc - calcite, Ar - aragonite, Wo - wollastonite, SiO₂ - quartz. Several high-temperature phases, not found in the samples studied, are shown for discussion of a possible mode of formation of the pseudomorphs: Lr - larnite, Ht - hatrurite, Sp - spurrite, and Tl - tilleyite

■ composition of the pseudomorphs - wet analysis of handpicked sample SNZ 1 (Table 3)

● microprobe analyses of the pseudomorphs, sample SN 44

△ theoretical composition of pseudomorphs after wollastonite following the carbonation reaction $\text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2$

Carbonation of wollastonite

The preservation of remains of the amorphous phase after wollastonite in the pseudomorphs indicate the following mode of formation of pseudomorphs after wollastonite:

two step alteration including: (1) transformation of wollastonite to optically and X-ray amorphous phase (which could probably result from a high-rate tectonic deformation or shock wave compression), (2) reaction of relatively unstable amorphous CaSiO₃ with CO₂, when exposed to water with high contents of CO₂, mainly in the zone of supergene alteration. The microscopic-scale deformations in wollastonite and the presence of abundant isotropic needles, which represent alteration products of former wollastonite indicate that this is the most probable mode of formation of the pseudomorphs. The carbon and oxygen isotopic compositions measured in the CaCO₃-rich pseudomorphs after wollastonite support the alternative of a late supergene carbonation.

Alternative modes of formation of the pseudomorphs, including, e.g., a spontaneous decomposition of wollastonite to CaO + SiO₂ (due to shock wave deformation) du-

ring the step (1) or high-temperature reaction of a part of wollastonite with calcite (from the enclosing marble) to larnite, spurrite, or other very high-temperature minerals (also an alternative of step 1) could not be supported by observation; no remains of CaO or larnite were observed. Leaching of untreated pseudomorph sample SN 44 in distilled water continuously charged with gaseous nitrogen resulted in pH 9.3 of the solution, indicating only a trace-level concentration of $(\text{OH})^-$ ions. Unstable high-temperature minerals formed from wollastonite would transform to CaCO_3 -rich pseudomorphs on exposure to water having a high content of CO_2 (step 2).

Single-step modes of formation of the pseudomorphs such as incongruent dissolution of wollastonite, and replacement by CaCO_3 , in the zone of weathering is not supported by observation - wollastonite behaviour as a mineral stable during weathering is well known. The associated diopside, quartz and primary calcite show no replacement by secondary calcite.

The most reasonable explanation for the formation of the wollastonite pseudomorphs is provided by two-step evolution mode, which is supported by the presence of the amorphous phase after wollastonite in the pseudomorphs. It is suggested that amorphous CaSiO_3 is susceptible to carbonation in the zone of weathering in contrast to crystalline wollastonite, for which no report of alteration under such conditions seems to exist. It is also noted that high resolution transmission electron microscopy, which could not be used in the course of this study, may provide a more conclusive information on mechanism of wollastonite transformation to the pseudomorphs.

Stable isotope and fluid inclusion study

Samples representing all distinct types of calcite observed in the Nezdice quarry and surroundings were selected for the stable isotope study. The description of individual samples and stable isotope data are given in Tab. 4.

Analytical methods

For the carbon and oxygen isotopic determination on carbonates the samples were reacted with 100% H_3PO_4 at 25 °C under vacuum (McCrea 1950). Carbon and oxygen isotopic determinations were performed on a Finnigan MAT 251 mass spectrometer. Results are expressed in usual δ notation relative to international V-PDB standard. The $\delta^{18}\text{O}$ values related to V-SMOW standard were derived by recalculation. Overall analytical error was ± 0.1 ‰ for both carbon and oxygen isotope determination.

Fluid inclusions were studied in cleavage flakes of calcite using optical microthermometrical methods of homogenization and cryometry on a CHAIXMECA heating and freezing stage, which enables observation of phase changes inside fluid inclusions in the temperature range from -180 °C to +600 °C. The apparatus was calibrated using MERCK chemical standards and the triple points of water and CO_2 .

Carbon and oxygen isotope composition

The carbon and oxygen isotope compositions of the samples of impure calcite marbles, are plotted in the $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ diagram shown in Fig. 2, and are shifted slightly from the field typical for non-metamorphosed limestones. This usual isotope shifts to lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are mostly related to decarbonation reactions. During high-temperature metamorphic reactions, the CO_2 that escapes from the metamorphosed rock sequence has slightly higher $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values than the original marble. As a result of this the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data of the residual marble are shifted to lower isotopic values (see Žák - Sztacho 1994, for review of literature related to this process and for data from other marble bodies in the Moldanubian unit). To trace this process in detail, a profile perpendicular to marble contact with granitic dyke was sampled and analysed (see data in Tab. 4 and analytical points in Fig. 2, connected by dashed line). Sample SN 64 which is more shifted to lower $\delta^{18}\text{O}$ values is influenced also by interaction with circulating hydrothermal fluids.

Samples of calcite from hydrothermal veins have a narrow range of $\delta^{13}\text{C}$ values but a very wide range of $\delta^{18}\text{O}$ values. Coarse/blocky hydrothermal calcite (sample SN 63) that completely fills open N-S trending fractures (width up to 8 cm) with crystals up to 6 cm in diameter have $\delta^{18}\text{O}$ value of +8.2 ‰ (SMOW). The highest homogenization temperature of fluid inclusions (see below) recorded in this type of calcite are as high as 180 °C. Calculated oxygen isotopic composition of hydrothermal fluids at this temperature is -2 ‰ (SMOW). Such a value is typical for waters with relatively shallow circulation in the crust which had undergone only partial oxygen isotope exchange with hot magmatic and/or metamorphic rocks or some type of waters derived from sedimentary basins.

The sample SN 64 showed $\delta^{18}\text{O}$ value of +18.1 ‰ (SMOW). Using the Th of fluid inclusions in this type of calcite, an oxygen isotopic composition of the fluid is calculated to be approximately of +3 ‰ (SMOW). This value is typical for waters with relatively shallow circulation in the crust that have undergone limited oxygen isotope exchange with hot magmatic and/or metamorphic rocks or it represents some type of water from sedimentary basins.

Carbon and oxygen isotopic compositions of recent calcite flowstone films deposited by meteoritic waters in karst systems (karstic-type waters) fit well into the typical field of cave carbonates of Bohemia.

Calcite (and aragonite) phase from CaCO_3 -rich pseudomorphs after wollastonite show oxygen isotopic composition similar to values typical for Bohemian cave carbonates (carbonates deposited from recent meteoric waters under temperature close to average surface year temperature). The oxygen isotopic composition of such calcite is controlled only by temperature and the oxygen isotopic composition of water that deposited the calcite. The oxygen isotopic composition of the marble has no influence.

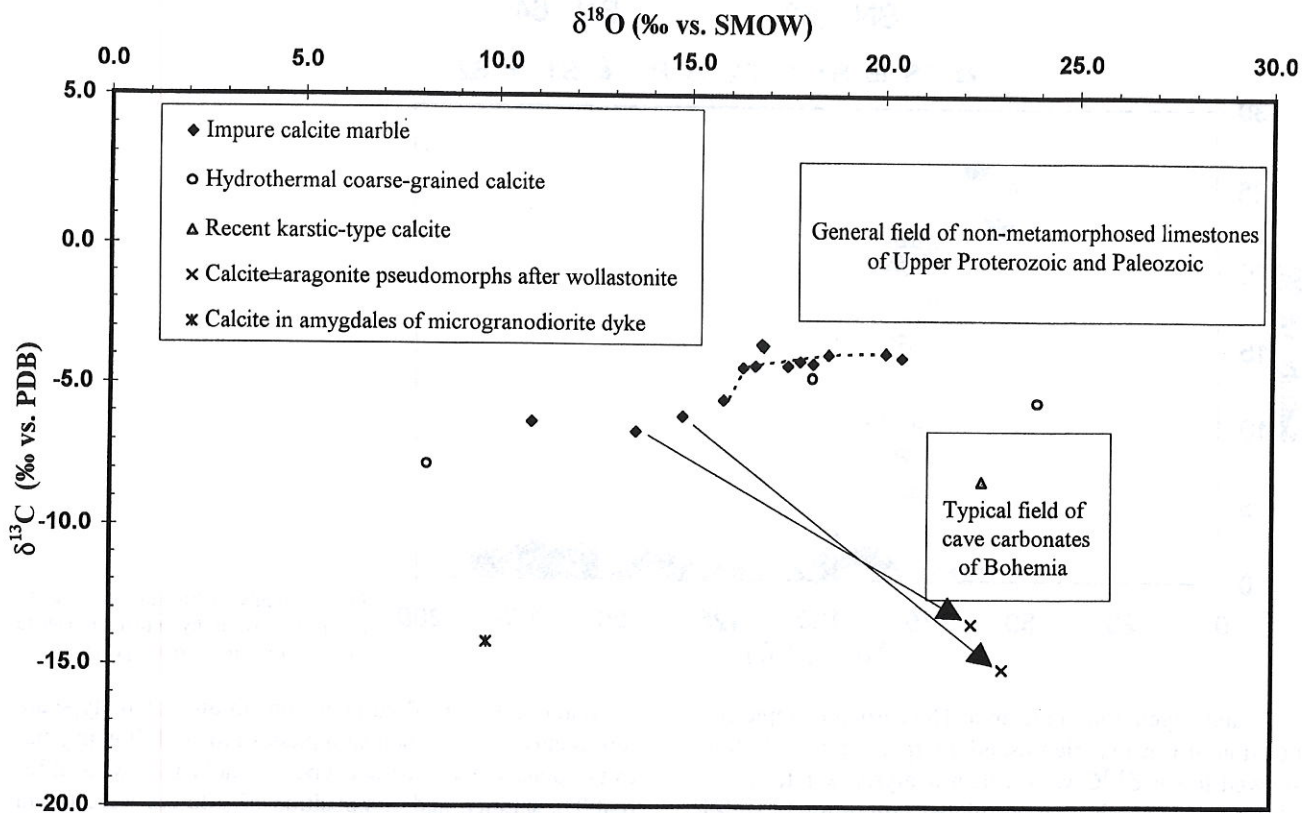


Fig. 2. Carbon and oxygen isotopic composition of carbonates from the Nezdice quarry. Data for marble and for calcite-rich pseudomorphs from the same sample are connected by an arrow

In contrast, the carbon isotopic composition of such calcite types results from mixing of carbon derived from the dissolved marble ($\delta^{13}\text{C}$ values close to -4‰) and car-

bon dioxide of soil origin, derived by the bacterial oxidation of organic matter in soils. The $\delta^{13}\text{C}$ values of soil CO_2 origin usually are about -25‰ and depend on the cli-

Table 4. Carbon and oxygen isotope data of carbonates

Anal. No.	Sample No.	Location	Sample description	$\delta^{13}\text{C}$ (PDB)	$\delta^{18}\text{O}$ (PDB)	$\delta^{18}\text{O}$ (SMOW)
1	SN 59	Nezdice quarry	Impure calcite marble, calcite replaced by chlorite and quartz	-4.3	-12.3	18.2
2	SN 60	Nezdice quarry	Porous impure marble showing hydrothermal alteration	-3.7	-13.6	16.9
3	SN 60	Nezdice quarry	The same sample, less altered zone	-3.6	-13.6	16.8
4	SN 62	Nezdice quarry	Colourless calcite crystals coating walls of N-S trending open fractures	-5.6	-6.7	23.9
5	SN 62	Nezdice quarry	Impure marble from the same sample	-4.3	-13.0	17.5
6	SN 63	Nezdice quarry	Coarse/blocky hydrothermal calcite completely filling open N-S trending fractures, crystals up to 6 cm, thickness of the vein 8 cm	-7.9	-22.0	8.2
7	SN 64	Nezdice quarry	Colourless calcite crystals coating walls of N-S trending open fractures	-4.8	-12.3	18.1
8	SN 64	Nezdice quarry	Impure marble from the same sample	-6.4	-19.4	10.9
9	SN 67	Nezdice quarry	Recent calcite flowstone films deposited by karstic-type waters	-8.4	-8.1	22.5
10	SN 66	Ostružno	Impure marble adjacent to granitic dyke, distance 15 cm from the contact	-3.9	-10.5	20.0
11	SN 66	Ostružno	The same sample, distance 3 cm from the contact	-3.9	-11.9	18.6
12	SN 66	Ostružno	The same sample, distance 2 cm from the contact	-4.3	-13.8	16.7
13	SN 66	Ostružno	The same sample, distance 1 cm from the contact	-4.4	-14.1	16.3
14	SN 66	Ostružno	The same sample, distance 0.5 cm from the contact	-5.6	-14.6	15.9
15	SN 70	Ostružno	Impure marble close to granitic dyke, another sampling site	-4.2	-12.7	17.8
16	SN 72	Nezdice quarry	White marble, usual type, less disturbed	-4.0	-10.1	20.4
17	SN 43	Nezdice quarry	Impure calcite marble (\pm diopside, wollastonite, phlogopite, quartz) with calcite pseudomorphs after wollastonite, calcite + aragonite pseudomorphs	-15.1	-7.6	23.1
18	SN 43	Nezdice quarry	The same sample, marble without pseudomorphs	-6.1	-15.6	14.8
19	SN 44	Nezdice quarry	Impure calcite marble (\pm diopside, wollastonite, phlogopite, quartz) with calcite + aragonite pseudomorphs after wollastonite, calcite pseudomorphs	-13.5	-8.3	22.3
20	SN 44	Nezdice quarry	The same sample, marble without pseudomorphs	-6.7	-16.8	13.6
21	SN 24	Kadešice	Augite microgranodiorite dyke with calcite-quartz-chlorite amygdalae, calcite from amygdalae	-14.3	-20.5	9.7

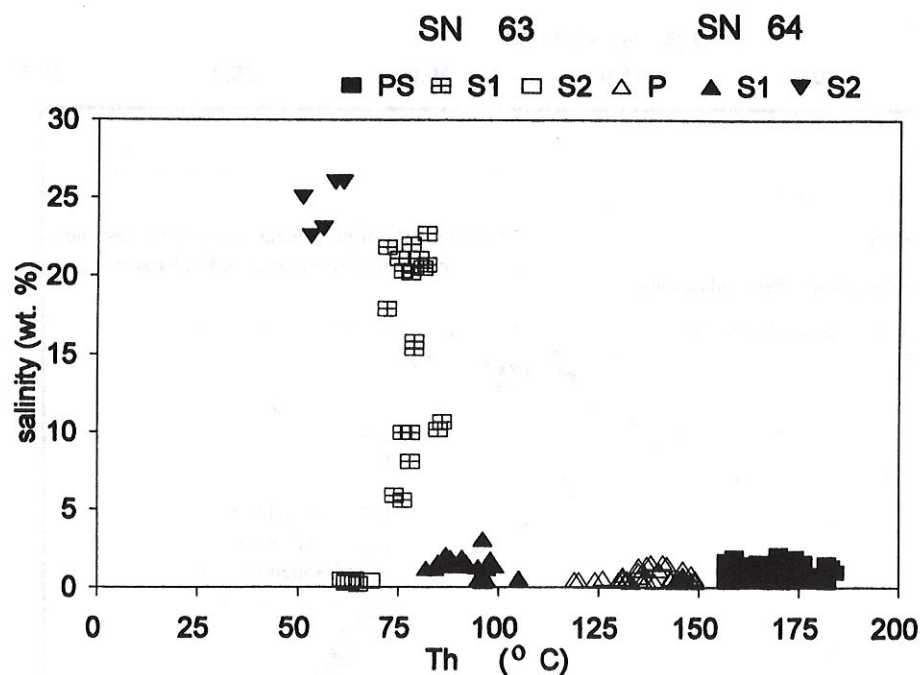


Fig. 3. Salinity vs. Th diagram for studied inclusions in hydrothermal calcite samples from the Nezdice quarry.

mate and vegetation in the area. The carbon isotopic composition of CaCO_3 -rich pseudomorphs after wollastonite showed lower $\delta^{13}\text{C}$ values than analysed karstic calcite. This can be a result of either higher proportion of soil-derived CO_2 in the pseudomorphs relative to karstic type calcite or by the formation of CaCO_3 forms in respective samples under different climatic conditions.

Fluid inclusions

Fluid inclusions were studied in three samples of hydrothermal calcite (SN 63 - vein type, SN 64 and SN 62 - calcite crystals coating walls of fractures).

Several genetic types of aqueous inclusions were observed in vein type of calcite (SN 63). The oldest inclusions, probably pseudosecondary (PS in Table 5 and Fig. 3), occur along short fluid inclusion planes and have consistent liquid to vapour ratio with 10 vol. % of vapour phase. Temperatures of homogenization (Th) vary between 157 and 184 °C, salinity is low, from 0.2 to 1.9 wt. % NaCl equiv. (after Bodnar 1993).

Later secondary fluid inclusions in this calcite type are represented as fluid inclusion planes mostly following cleavage planes. Two distinct types of inclusions with different Th, salinity, and composition of solution were found (S1 and S2). While S2 inclusions have Th from 62 to 68 °C and low salinity from 0.2 to 0.5 wt. % NaCl equiv., S1 inclusions have higher Th between 72 and 92 °C and salinity is in the range from 5.6 to 22.7 wt. % NaCl equiv. The temperatures of melting of hydrohalite ($T_{m_{hh}} = -23.6$ to -23.9 °C) and temperatures of eutectic (Te) between -52.1 and -55.2 °C in inclusions with higher salinity indicate $\text{H}_2\text{O-NaCl-CaCl}_2$ fluid composition with up to 7 wt. % of CaCl_2 and 10 wt. % of NaCl. This can indicate an influx of later high salinity fluid with greater content of CaCl_2 .

Analogous aqueous inclusions occur in calcite crystals of sample SN 64. Primary and pseudosecondary inclusions (small three-dimensional clusters or short fluid inclusion planes, P in Table 5 and Fig. 3) have more or less consistent liquid to vapour ratio with about 10 vol. % of vapour phase. Th ranges from 119 to 149 °C, salinity is low, from 0.2 to 1.7 wt. % NaCl equiv.

Table 5. Fluid inclusion data of hydrothermal calcites

Sample No.	Genetic type of inclusions	Th (°C)	Te (°C)	$T_{m_{hh}}$ (°C)	$T_{m_{ice}}$ (°C)	Salinity (wt. % NaCl equiv.)	NaCl (wt. %)	CaCl_2 (wt. %)
SN 62	S					0.9 - 1.2		
SN 63	PS	157 - 184				0.2 - 1.9		
	S1	72 - 92	-52.1 to -55.2	-23.6 to -23.9	-3.4 to -20.4	5.6 - 22.7	6 - 10	4 - 7
	S2	62 - 68				0.2 - 0.5		
SN 64	P	119 - 149				0.2 - 1.7		
	S1	74 - 105	-37.0			0.2 - 3.1		
	S2	51 - 63	-39.0 to -59.0	-15.6 to -22.3	-20.2 to -25.6	22.5 - 26.0	12 - 14	12

Explanation: Th - temperature of homogenization, Te - temperature of eutectic, $T_{m_{hh}}$ - temperature of melting of hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$), $T_{m_{ice}}$ - temperature of melting of ice, P - primary inclusions, PS - pseudosecondary inclusions, S - secondary inclusions

Two generations of secondary inclusions (S1 and S2) with different Th and salinity were observed in sample SN 64. The S1 inclusions have Th from 74 to 105 °C and salinity from 0.2 to 3.1 wt. % NaCl equiv. In contrast, the S2 inclusions are characterized by Th from 51 to 63 °C and high salinity between 22.5 and 26 wt. % NaCl equiv. The Te temperatures in S2 inclusions ranging from -37.0 to -59.0 °C suggest that the solutions consist of CaCl₂ and NaCl with possible minor MgCl₂ and KCl admixture (Borisenko 1977).

In colourless calcite crystals of sample SN 62 virtually secondary only single-phase liquid-only aqueous inclusions were found with salinity from 0.9 to 1.2 wt. % NaCl equiv. Much higher δ¹⁸O values of this calcite type probably reflect notably lower temperatures of deposition close to 60-70 °C.

Discussion

Numerous studies of wollastonite-bearing assemblages from areas of high-grade metamorphism and contact metamorphic environments indicate that wollastonite persists (metastably, in part) under conditions of decreasing temperatures up to conditions of surficial weathering, without noticeable alteration.

Harker and Tuttle (1956) succeeded in reversing the wollastonite reaction: $\text{CaCO}_3 + \text{SiO}_2 \rightleftharpoons \text{CaSiO}_3 + \text{CO}_2$ under moderate temperatures by introducing CO₂ into experimental charges. It is therefore surprising that examples of natural reversal are seldom reported. Harley and Santosh (1995) described wollastonite carbonation which took place under conditions of high-grade metamorphism and CO₂ influx from an abyssal source. Composition of the granular mosaic of calcite and quartz replacing wollastonite in Kerala samples corresponds approximately to stoichiometry of the reversed wollastonite reaction.

The pseudomorphs described from Nezdice do not correspond to this mode of formation by having a very fine-grained texture (<1 μm), by deviating strongly from stoichiometry of the carbonation reaction (desilication), by the presence of aragonite besides calcite in one sample, by weathering profile signature of the oxygen and carbon isotopes in carbonates in the pseudomorphs, and by the presence of an amorphous phase after wollastonite.

An acceptable scenario is provided by a two-step evolution mode. An amorphous alteration product of wollastonite accompanies secondary carbonates and minor SiO₂ in the pseudomorphs. It is suggested that the optically isotropic and probably X-ray amorphous phase after wollastonite is the unstable phase which reacted to secondary carbonates in the zone of weathering. The isotope information on secondary carbonates indicates that late stages of evolution of the pseudomorphs correspond to supergene (near surface weathering) alterations.

Aragonite is present in pseudomorphs after wollastonite in sample SN 44 (Table 1), showing effects of weathering. However, as morphological position of aragonite in

the wollastonite pseudomorphs is unknown, conditions of its crystallisation are unclear.

Among the different types of calcite samples studied, only the recent flowstone films have carbon and oxygen isotopic composition similar to the calcite + aragonite pseudomorphs after wollastonite. Hydrothermal calcite veins exhibit very wide range of oxygen isotope data because of the involvement of several fluid types and gradual temperature drop. Nevertheless, none of these hydrothermal fluids could produce studied pseudomorphs after wollastonite.

Hydrothermal vein calcites formed under relatively wide thermal conditions. The vein type (sample SN 63) formed at temperatures from 160 up to 190 °C and calcite crystals coating walls of open fractures at temperatures 120 to 150 °C (SN 64), and 60 to 70 °C (SN 62). Salinity of early fluids was low to moderate, from 0.2 to 2 wt. % NaCl equiv.

On the contrary, later penetrating fluids, characterized by secondary fluid inclusions, had high salinity up to 26 wt. % and greater content of CaCl₂. Similar fluid types were recorded at numerous localities of post-Variscan fluid circulation in western part of the Bohemian Massif (Behr et al. 1993, Dobeš et al. 1995) and are related to shallow to moderate depths of fluid circulation in the crust, not related to Variscan magmatic and metamorphic events.

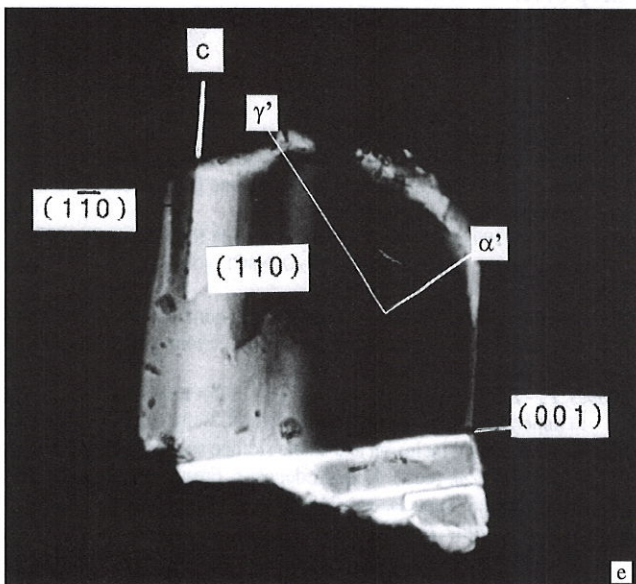
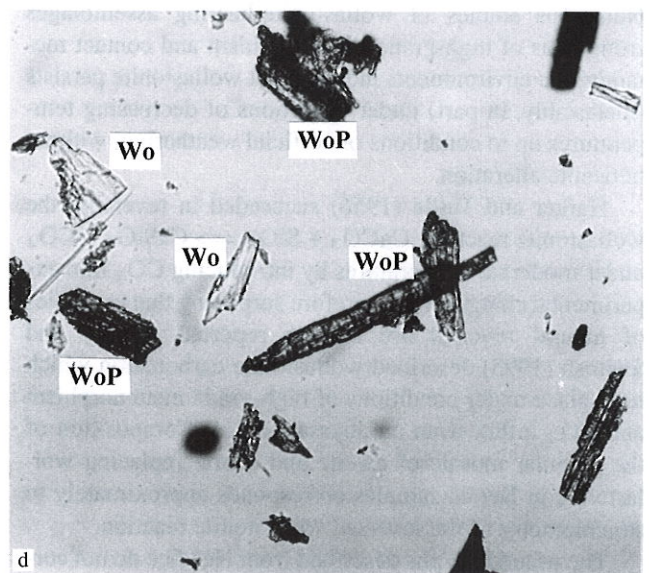
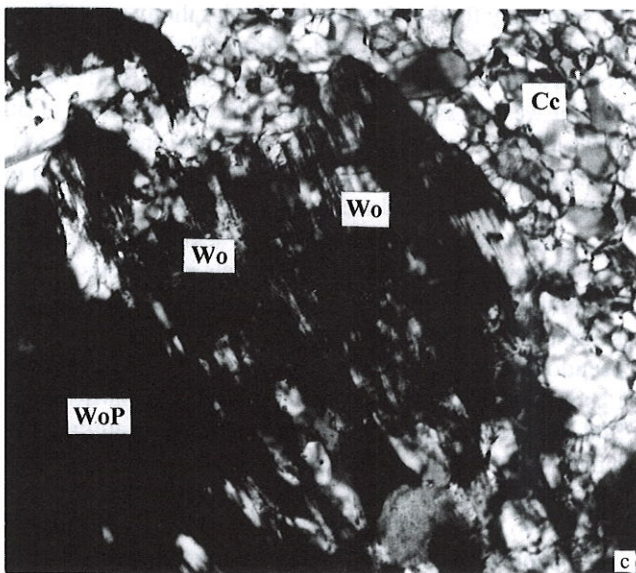
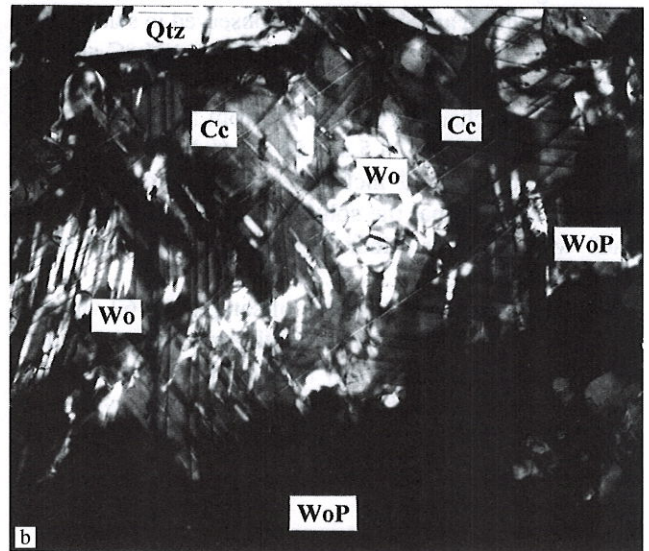
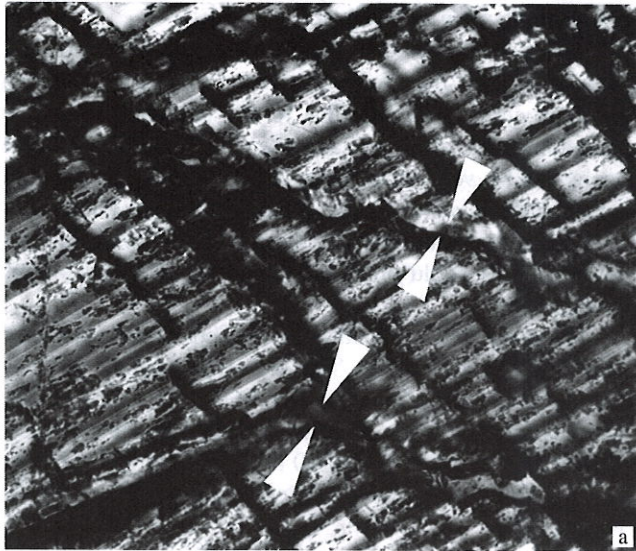
Acknowledgements. We wish to acknowledge the X-ray diffraction identification of minerals in two samples by J. Hloušek, electron microprobe analyses done by Z. Kotrba and I. Vavřín, and the wet chemical analysis of the pseudomorph sample by the staff of the Chemical Laboratory of Czech Geological Survey, in particular J. Šikl. The authors gratefully acknowledge the helpful comments of D. Leach. This work was supported in part by U.S.- Czech Science and Technology Joint Fund under project No. 94017 and by Czech Geological Survey, project "Geological model of western Bohemia in relation to deep borehole KTB in FRG".

Submitted November 20, 1996

References

- Behr, H. J. - Gerler, J. - Hein, U. F. - Reutel, Ch. J. (1993): Tectonic Brines und Basement Brines in den Mitteleuropäischen Varisziden: Herkunft, metallogenetische Bedeutung und geologische Aktivität. - Göttinger Arb. Geol. Paläont., 58, 3-28.
- Bodnar, R.J. (1993): Revised equation and table for determining the freezing point depression of H₂O-NaCl solutions. - Geochim. Cosmochim. Acta, 57, 683-684.
- Borisenko, A. S. (1977): Determination of salt composition of the solutions of fluid inclusions in minerals using cryometry. (In Russian) - Geol. Geofyz., 8, 16-28. Novosibirsk.
- Dobeš, P. - Žák, K. - Viets, J. - Leach, D. (1995): Epithermal Pb-Zn vein mineralization of the Stříbro ore district, Bohemian Massif, Czech Republic: Fluid inclusion and stable isotope study. In: J. Pašava - B. Kříbek - K. Žák (eds.): Mineral deposits: From their origin to their environmental impacts, 345-348. Balkema. Rotterdam.
- Harker, R. I. - Tuttle, O. F. (1956): Experimental data on the P CO₂ - T curve for the reaction: calcite + quartz = wollastonite + carbon dioxide. - Amer. J. Sci., 254, 239-256.
- Harley, S. L. - Santosh, M. (1995): Wollastonite at Nuliyam, Kerala,

K. Žák - P. Dobeš - S. Vrána: Formation conditions of various calcite types and unusual alteration products of wollastonite in calcite marble near Nezdice (Varied Group of Moldanubicum), Czech Republic (Pl. I)



- southern India: a reassessment of CO₂-infiltration and charnockite formation at a classic locality. - *Contr. Mineral. Petrology* (in press).
- Krs, M. - Vrána, S. (1993): Palaeomagnetism and petromagnetism of auge microgranodiorite, Nezdice near Kašperské Hory, southern Bohemia. - *J. Czech Geol. Soc.*, 38, 201-207.
- Lellák, J. (1993): Metalogenesis of the Kašperské Hory ore district. - Ph.D. thesis. (In Czech) - MS Faculty of Sci., Charles University, Praha.
- McCrea, J. M. (1950): On the isotopic chemistry of carbonates and a paleotemperature scale. - *J. Chem. Phys.*, 18, 849-857.
- Pertoldová, J. (1993): Petrological and mineralogical study of the Kašperské Hory deposit. In: M. Punčochář et al. (1993): Final report from the project of Au-W ore exploration in Kašperské Hory. (In Czech) - MS Geofond Praha.
- Žák, K. - Sztacho, P. (1994): Marbles, calc-silicate rocks and skarns of the Moldanubian unit (Bohemian Massif, Czechoslovakia): Carbon and oxygen isotope and fluid inclusion constraints on formation conditions. In: Proceedings of the 29th International Geological Congress, Part A.: T. Nishiyama - G. W. Fisher (eds.): Metamorphic reactions: Kinetics and mass transfer, 39-49. VSP Publishers, Zeist.

Podmínky vzniku různých typů kalcitu a pseudomorfóz po wollastonitu v kalcitickém mramoru u Nezdic (pestrá skupina moldanubika)

V lomu u Nezdic v jihozápadních Čechách jsou odkryté wollastonitem bohaté polohy v kalcitickém mramoru s poměrně rozsáhlou přeměnou wollastonitu v sekundární pseudomorfózy. Protože přírodní výskyty zpětného průběhu wollastonitové reakce jsou vzácné, byly tyto pseudomorfózy podrobeny mineralogickému a izotopickému studiu. Pro srovnávací účely a pro interpretaci způsobu vzniku pseudomorfóz byly s použitím analýzy stabilních izotopů studovány vzorky mramoru ze zóny metamorfni dekarbonizace, kalcit hydrotermálních žil a povlaky kalcitu vzniklé během subrecentního krasovění. Studium fluidních inkluzí v hydrotermálním kalcitu poskytlo informace o teplotách a složení příslušných fluid. Získaná data nasvědčují dvouetapovému vývoji pseudomorfóz: (1) přeměna wollastonitu v opticky izotropní a pravděpodobně rentgen-amorfní fázi; možnou příčinou této neobvyklé transformace by mohla být tektonická deformace (s vysokým podílem deformace v čase) nebo deformace šokovou vlnou, (2) reakce relativně nestabilní amorfní fáze s vodou obsahující zvýšenou koncentraci HCO₃⁻, produkující CaCO₃; izotopické složení O a C nasvědčuje uplatnění této reakce v zóně zvětrávání, za účasti CO₂ vznikajícího půdní oxidací organických látek. Zatlačování izotropní fáze po wollastonitu sekundárními karbonáty (převážně kalcit, zčásti i aragonit) probíhalo s částečným odnosem křemíku a výsledné pseudomorfózy jsou značně bohatší CaCO₃, než by odpovídalo reakci CaSiO₃ + CO₂ = CaCO₃ + SiO₂. Zbytky izotropní fáze po wollastonitu se ještě vyskytují uvnitř pseudomorfóz. Alternativní způsoby vzniku pseudomorfóz, zahrnující např. spontánní transformaci wollastonitu na směs CaO + SiO₂ [hypotetický účinek šokové vlny, jakožto alternativa etapy (1)], nebo vysokoteplotní reakci části wollastonitu s okolním kalcitem v mramoru [rovněž alternativa etapy (1)] na larnit, spurrit nebo jiné velmi vysokoteplotní minerály, nenacházejí podporu v pozorování; nebyly zjištěny zbytky CaO nebo larnitu. Takovéto alternativní produkty by také reagovaly s HCO₃⁻ ve vodě na CaCO₃ (+SiO₂). Dosavadní literární data o chování wollastonitu v zóně zvětrávání nenavědčují možnosti vzniku pseudomorfóz inkongruentním rozpouštěním wollastonitu - tento minerál se chová v podmínkách zvětrávání jako značně stálý. Sdružený diopsid, křemen a kalcit nejsou postiženy zatlačováním sekundárními karbonáty. Analýzy stabilních izotopů a studium fluidních inkluzí v krystalech hydrotermálního kalcitu narostlých na trhlinách v mramoru svědčí o tom, že jejich vznik nemá spojitost se vznikem pseudomorfóz po wollastonitu.

← Explanation of plate I

- Deformed calcite in wollastonite marble, sample SN 43. The NW trending fractures (darkened), parallel to (10 $\bar{1}$) are displaced by the NE trending cleavage. Irregular open fractures are filled by younger calcite (indicated by arrows). Single polarizer. Width of the area shown 0.6 mm,
- Thin prisms of wollastonite (Wo, white, near centre), enclosed in calcite (Cc) are preserved unaltered. Former wollastonite aggregate in the lower part is completely altered to isotropic pseudomorph material (WoP). Sample SN 44. Crossed polarizers. Width of the area shown 1.8 mm,
- Wollastonite in the large central aggregate (Wo) is of a mottled appearance and shows incipient alteration. Former wollastonite in lower left is completely altered to isotropic pseudomorph material (WoP); granular mosaic of calcite (Cc) in upper right. Sample SN 44. Single polarizer. Width of the area shown 1.8 mm,
- Fresh transparent wollastonite (Wo) and grey, isotropic pseudomorphs after wollastonite (WoP) in immersion liquid. The longest pseudomorph is deformed and shows notch-like recessions. Insoluble residue after leaching of sample SNZ 1 in 9 % HCl. Single polarizer. The largest pseudomorph fragment is 0.10 mm long,
- Deformation glide twinning of diopside on (001). The two lighter lamellae at the base are moved towards observer. The crystal fragment, 70 μ m long, is mounted in immersion liquid. Sample SN 44. Crossed polarizers,
- Centrally positioned diopside (Di) shows several interference fringes corresponding to individual dislocations bounding disoriented portions (hence with variable birefringence) of a former single crystal of diopside. Calcite (Cc) and wollastonite (Wo) are present next to diopside. Wollastonite developed notable mosaicism and interference fringes, not visible in this figure. Sample SN 43. Crossed polarizers. Width of the area shown 1.5 mm