

7. Petrological study of CO₂ industrial emission bonding in minerals via artificial carbonatization of metaperidotite

MARTIN RADVANEC

State Geological Institute of Dionýz Štúr, RC Spišská Nová Ves, Markušovská cesta 1, Slovak Republic

Abstract. The part extends an experimental base for possibility to store the carbon dioxide emission via artificial carbonatization of metaperidotite bodies located in the East Slovakia near Hodkovce village. Three types of hydrated mantle rocks, metaperidotite (metalherzolite), metawehrlite and metawebsterite were subjected to reaction with water and CO₂ and there from obtained suspensions were heated under different temperatures of 50 °C, 160 °C and 200 °C in the laboratory conditions. From the heated suspensions the acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite) and carbonates (calcite, dolomite, magnesite) were formed and confirmed by X-ray analyses. According to the mass balance calculations between the source silicate minerals (serpentine) and new carbonates-products, the mass from 1,070 kg to 1,429 kg of CO₂ can be sequestered in 1 m³ of the source metaperidotite.

Key words: CO₂ disposal, artificial carbonatization, acid carbonates, carbonates, CO₂ storage capacity, meta-peridotite, serpentinite

7.1. Introduction

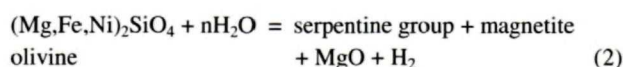
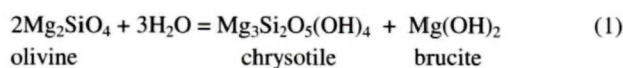
The main sources of gases migrating to the atmosphere, including carbon dioxide that contributes to the greenhouse effect, derive from not only the high-emission technological processes, but also from other natural processes occurring on the surface and in the Earth's interior. Nowadays it is estimated that carbon dioxide concentration in the Earth's atmosphere has increased from 290 to 370 ppm during the last 150 years (Etherides et al. 1996; Drobek et al., 2008). The scientific evidence is now overwhelming: climate change presents very serious global risk and it demands an urgent global response. The method to remove the anthropogenous carbon dioxide is a sequestration, understood as capture or separation, transport and storage of the CO₂ emission in the deep geological structures. CO₂ sequestration methods are divided into:

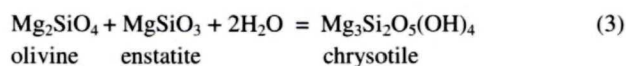
- biological – intake through biosphere (photo-synthesis),
- physical – through storage in the ocean and deep geological structures; frequently proposed storage locations are exhausted hydrocarbons deposits (oil and natural gas), saline caverns or deep-lying brine water bearing strata, less frequently non-mined or not-balanced hard coal beds. This technology provides permanent prevention of carbon dioxide emission escaping to the atmosphere, while the monitoring of CO₂ leakages from the CO₂ stored deposit has to be continuous.
- chemical – by mineral carbonatization (“mineral sequestration”), consisting in binding CO₂ with minerals.

The mineral CO₂ sequestration is not so preferred in comparison to deposition in regional aquifers, or depleted hydrocarbon deposits. However it is concerned to be one of the approaches which can be helpful in the combat climate change (Schiller, 2006; Uibu, 2008).

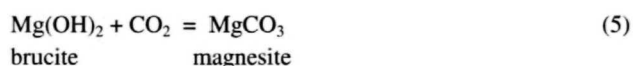
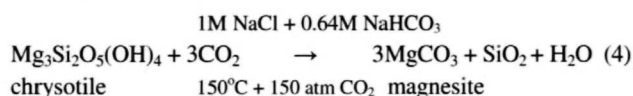
Serpentinite has been proposed as an efficient reagent for CO₂ sequestration by reason that the highly magnesium serpentinite or forsteritic olivine favours the reaction to magnesite in hydrated mantle rocks (Deer et al., 1997). This reaction simultaneously allows deposition of the carbon dioxide in the serpentinite using its unnatural carbonatization (Herzog, 2002; Bochenczyk et al., 2007; Drobek et al., 2008). The final product of carbonatization is acid group of carbonates (nesquehonite, barringtonite, dypingite and hydromagnesite) as well as group of carbonates (calcite, dolomite, and magnesite) and silica. These minerals are stable without a negative effect on the environment (Lackner et al., 1995; Voormeij & Simandl, 2004; Dunsmore, 1992).

Serpentinite is formed by hydration of olivine and enstatite at variable depths in the Earth's crust or mantle during regional metamorphism. Alternatively, it can be formed by water alteration at the surface in conformity with reactions 1, 2, and 3 (Johannes, 1968; Martin & Fyfe, 1970; Malakhov, 1971):





According to the exchange reactions 4 and 5 the serpentine group (chrysotile) reacts with CO_2 to produce magnesite during its carbonatization in atmosphere conditions (Herzog, 2002, Drobek et al., 2008). However a process of artificial carbonatization uses NaCl and NaHCO_3 to produce intermediate product of $\text{MgCl}_2 + \text{Mg}(\text{OH})_2$ and, consequently, the final carbonatization follows reactions:



In term of reaction 4 is deducible, that for sequestration of 1 tonne of CO_2 is necessary to utilize a mass of 2.1 to 3.18 tonnes of serpentinite, in conformity with its density (Herzog, 2002). Both reactions (4 and 5), in agreement with numerous experimental works, irreversibly change the serpentine group of minerals (chrysotile, antigorite, lizardite) to carbonates. Serpentinite bodies are therefore efficient in CO_2 storage. Those bodies which were not influenced by natural CO_2 during metamorphism, or exhumation, are suitable for the artificial carbonatization purposes. Therefore a mineralogical and petrological study of the bodies is needed, because their results are crucial to select a suitable body in the mineral sequestration methodology.

There are several occurrences of partially or completely serpentinitised metaperidotites bodies in the Slovak Republic. A targeted research for asbestos-lizardite occurrence was carried out at the sites Jaklovce, Sedlice, Dobšiná, Breznička - Kalinovo, Komárovce - Hodkovce, Rudník and Jasov in the past (Zlocha & Hovorka, 1971, Zlocha, 1980, Grecula et al., 1995). These bodies are almost completely serpentinitised and accompanied with variable content of carbonate finds (Hovorka et al., 1985). It means that their evaluation for calculations of carbon dioxide sequestration requests detailed mineralogical and petrological study. However this is not the only criterion for usable serpentinite body, but its volume, depth, morphology and tectonic structure are certainly important as well (Fig. 1.1).

A dominant CO_2 producer in Slovakia is US STEEL Ltd. with annual production of more than 11 Mtons per year. The surrounding of this plant from the geological point of view is suitable for CO_2 storage by various methods. The area near the producer is the largest ultramafic body of metaperidotite, with extension about several km^3 . The outcrop of metaperidotite is located near Hodkovce. In addition to the Komárovce – Hodkovce large body, there is located small metawebsterite body near Rudník and the metawehrlite body near Jasov, both having several 100 m^3 in size (Zlocha, 1980). Encouraging of body circumstances in the depth is confirmed by a high temperature gradient in Komárovce – Hodkovce metaperidotite body because the

reactions 4 and 5, which transform serpentinite to carbonates, have an optimum temperature interval from 70 to 130°C . A temperature of 59°C has been measured in the depth below 1,500 m in the borehole KO-1 near Komárovce (Biela, 1978; Franko et al., 1995).

The aim of this study is to test the mantle rocks capability (metaperidotite, metawehrlite, metawebsterite), selected from the East Slovakian area for permanent carbon dioxide liquidation by artificial carbonatization. A consistent bonding of CO_2 in crystal lattice of carbonates is sustained and ecological solution for CO_2 mitigation purposes (Goldberg et al., 2000; Herzog, 2002; Kelemen & Matter, 2008).

7.2. Mineral composition of source mantle rocks

The serpentinitised mantle-derived rocks were studied at the locality Hodkovce (samples HO-1, HO-2 and HO-3, metaperidotite). The minerals of serpentine group prevail over former magmatic mineral association (olivine and pyroxenes). Therefore it is possible to classify all the rocks studied as serpentinite.

Metaperidotite is formed by chrysotile (78 vol. % or 80%), olivine + enstatite + diopside (13%, or 10%), calcite and dolomite (1.3% or 0.4%), magnetite and hematite (8% or 9%). In the both samples the content of Cr-spinel is less than 0.5%. Moreover, it is possible to recognize hornblende, hornblende – pargasite, tremolite, Ni-sulphides and talc in accessory quantity.

7.3. Sample preparation and analytical conditions

Polished thin sections of source metaperidotite were studied under polarizing microscope. We have focused in the identification and volumetric evaluation of mineral phases. The composition of mineral association was measured by means of electron microprobe, Cameca SX-100, installed in the laboratory of the State Geological Institute of Dionýz Štúr, Bratislava. The microprobe was operated with accelerating voltage 15 KV, sample current 5-20 nA and the size of beam diameter varied from 5 to $20 \mu\text{m}$ in relation to the measured mineral. The counting time was 10 s and for fluorine 25 s. The following calibration standards were used: Ca-wollastonite, Mn-rhodonite, Na-albite, K-orthoclase and Cr-chromite., Ti-TiO₂, Al-Al₂O₃, Fe-fayalite, Mg-MgO and F-BaF₂. Detecting limit for individual elements was less than 0.05 wt.% with mistake 1σ .

For the X-ray and chemical composition study, the rocks were firstly pulverized below 1 mm, homogenized and quartered. Homogeneous fraction was analyzed by X-ray diffractive inspection in the laboratory of the State Geological Institute of Dionýz Štúr, Košice and silicate analyses were obtained by differential thermogravimetric analysis (Tuček et al., 2009).

Experimental study has been conducted at this way dressed samples. The serpentinite was mixed with water and carbon dioxide according to the procedure used by

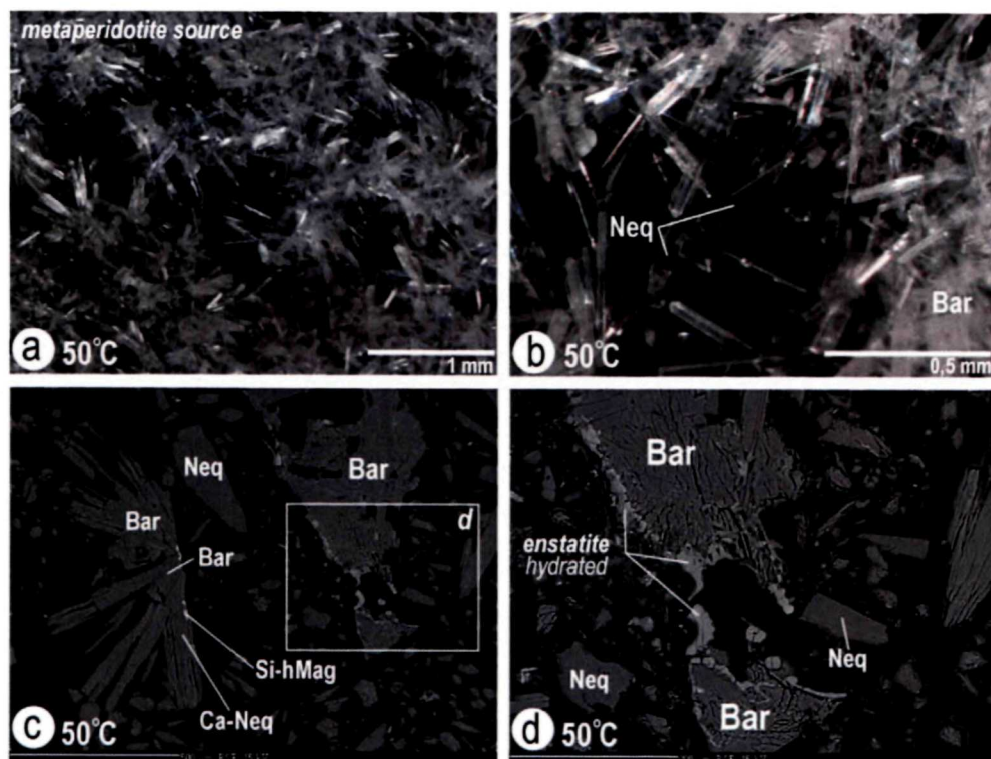


Fig. 7.1. Nesquehonite (Neq) and barringtonite (Bar) were formed during artificial carbonatization process at temperature 50 °C from the metaperidotite - serpentinite source. Sample HO-1, a) idiomorphic crystals of nesquehonite in binocular loupe, b) idiomorphic crystals of nesquehonite and barringtonite in binocular loupe, c) idiomorphic crystals of nesquehonite, barringtonite, Ca - nesquehonite (Ca-Neq) and Si hydromagnesite (Si-hMag). Back-scattered electron image, d) detail-c relic of hydrated enstatite and new barringtonite and nesquehonite. Back-scattered electron image.

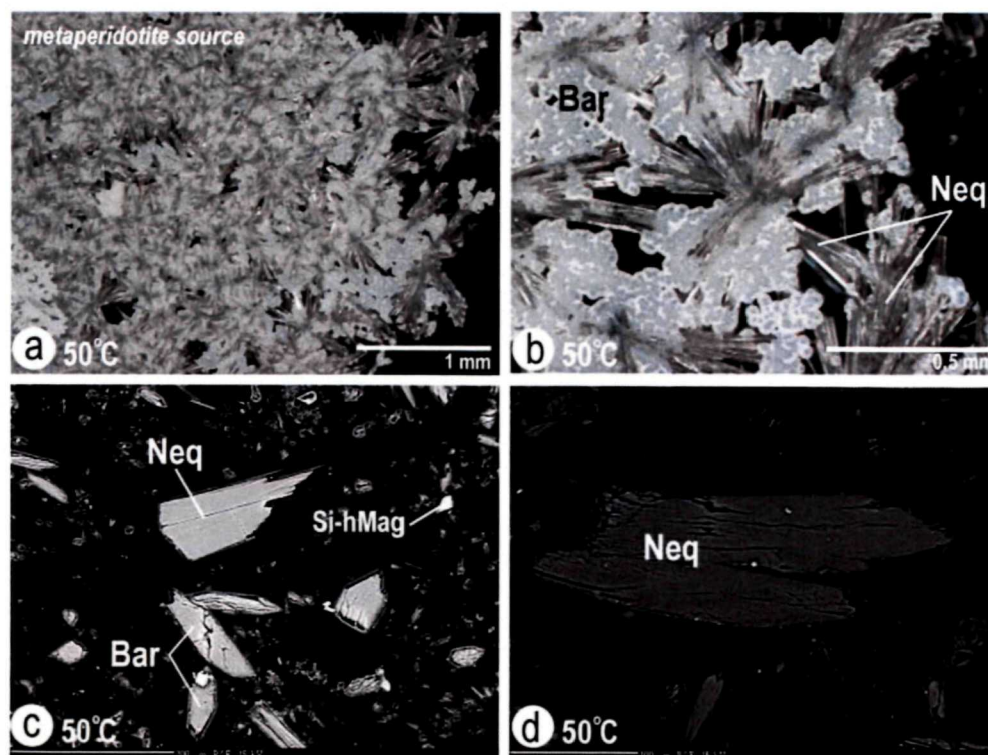


Fig. 7.2. Nesquehonite, (Neq), barringtonite (Bar) and hydromagnesite (hMag) formed by the artificial carbonatization process at temperature 50 °C from the metaperidotite - serpentinite source. Sample HO-2, a) nesquehonite and barringtonite in binocular loupe, b) nesquehonite and barringtonite in binocular loupe; c) nesquehonite, barringtonite, Ca and Si hydromagnesite (Si-hMag). Back-scattered electron image, d) nesquehonite in back-scattered electron image.

Tuček et al., (2009). Stable temperature 22 °C and CO₂ pressure from 0.1 to 0.3 MPa were maintained during controlled reaction from 5 to 20 hours. Leachates, with pH value about 8, became the source medium from which new products formed at temperatures 50 °C, 160 °C and 200 °C. The crystallization time was 4-24 hours. The new-formed and crystallized products were studied by optical methods and were analysed and controlled by the electron microprobe, by CHA (chemical silicate analysis), RTG (X-ray diffraction analysis), by DTA (differential thermic analysis) and by DTG (differential thermogravimetric analysis) where the almost end-member of acid carbonates and carbonates were found.

The photos of artificial carbonatization products were taken under binocular. The polished thin sections of reaction products were prepared and studied in optical microscope, as well. The chemical composition of new minerals was determined by spot electron microprobe analysis.

7.4. Minerals of artificial carbonatization formed at temperature 50 °C

A homogeneous idiomorphic nesquehonite or aggregations of nesquehonite and barringtonite up to size almost 1 mm were extracted from the suspension (serpentinite + CO₂ + H₂O) after reaction, filtration and crystallization from the filtrate (Fig 7.1 and 7.2). During the experiment the original source rock - metaperidotite was under constant temperature of 50 °C. A mixture of radially or omnidirectionally aligned nesquehonite was formed from the original metaperidotite. The nesquehonite and barringtonite were sporadically fibrillated by a hemisphere of hydromagnesite (Fig. 7.1c and 7.2c).

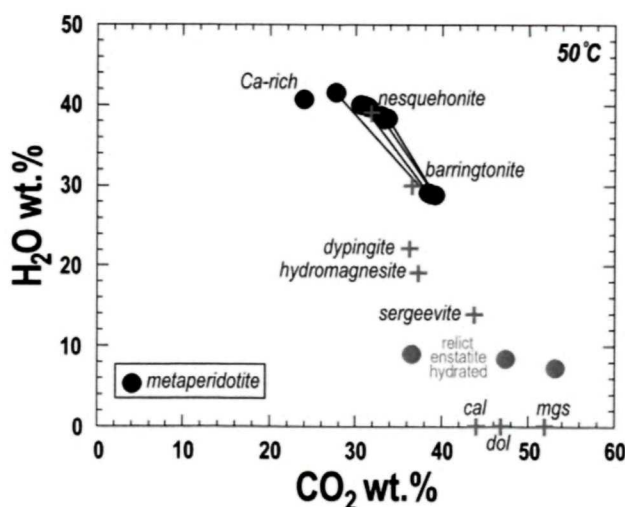


Fig. 7.3. Contents of H₂O and CO₂ in coexisting pair of nesquehonite - barringtonite (sample HO-1 and HO-2; metaperidotite source). These acid carbonates crystallized from the suspension (serpentinite + CO₂ + H₂O) during artificial carbonatization controlled by temperature 50 °C. Grey plus - contents of H₂O and CO₂ in end member minerals: cal - calcite, dol - dolomite, mag - magnesite. Grey circles - contents of H₂O and CO₂ in hydrated relic of enstatite.

Nesquehonite has almost identical values of X-ray diffraction profile and mineral lattice parameters as published in ASTM table values from the year 1974.

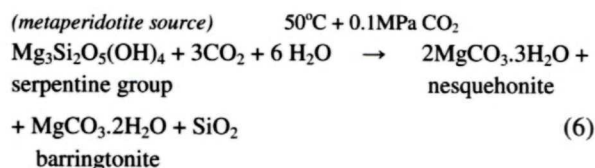
The chemical formula of nesquehonite is Si_{0.001}Fe_{0.001}Cr_{0.001}Ca_{0.002}Mg_{0.995}(HCO₃)(OH).2H₂O; barringtonite K_{0.001}Ca_{0.001}Mg_{0.999}CO₃.2H₂O and hydromagnesite (K_{0.003}Na_{0.003}Si_{0.099}Al_{0.012}Fe_{0.005}Cr_{0.025}Ca_{0.083}Mg_{4.772})₅(CO₃)₄(OH)₂.4H₂O (Fig. 7.3, Tab. 7.1).

Table 7.1. Representative analyses of acid carbonates formed during artificial carbonatization by temperature 50 °C. Neq-nesquehonite, Bar-barringtonite.

Sample	HO-1	HO-1	HO-2	HO-1	HO-2
Mineral	Neq	CaNeq	Neq	Bar	Bar
Rock	peridotite	peridotite	peridotite	peridotite	peridotite
Temper.	50 °C	50 °C	50 °C	50 °C	50 °C
SiO ₂	0.06	0.29	0.09	0	0.02
TiO ₂	0	0	0	0	0
Al ₂ O ₃	0	0.09	0	0	0
Cr ₂ O ₃	0.06	0.08	0.03	0	0
FeO	0	0.03	0.07	0	0.02
MnO	0	0	0.02	0	0.01
MgO	28.33	17.63	29.59	32.48	32.18
CaO	0.03	17.11	0.04	0.04	0
Na ₂ O	0	0.06	0	0	0.04
K ₂ O	0	0.01	0	0.04	0
Cl	0	0.08	0	0	0
H ₂ O*	38.20	40.67	39.98	29.08	28.83
Total	66.69	76.05	69.82	61.64	61.10
CO ₂ *	33.31	23.95	30.18	38.36	38.90
Total *	100	100	100	100	100
O	4	4	4	3	3
Si	0.001	0.006	0.002	0	0
Al	0	0.002	0	0	0
Ti	0	0	0	0	0
Cr	0.001	0.001	0.001	0	0
Fe	0	0.001	0.001	0	0
Mg	0.995	0.580	0.992	0.999	0.998
Mn	0	0	0	0	0
Ca	0.001	0.405	0.001	0.001	0
Na	0	0.001	0	0	0.002
K	0	0	0	0.001	0
Total	0.998	0.998	0.997	1.001	1.000
CCl	0	0.006	0	0	0
OH	6	5.987	6	4	4

* calculated from chemical formula, CO₂ = 100 - Total *

Nesquehonite and coexisting barringtonite crystallized from the metaperidotite source after the reaction of serpentinite with a mix of the water and carbon dioxide according to the reaction 6. This reaction was derived from the relation between main responsive mineral in metaperidotite (chrysotile) and new originated minerals (nesquehonite, barringtonite). The reaction 6 precisely compares cations and anions balance in chemical formulas of minerals (Tab. 7.1). Low element contents were omitted in chemical formulas.



The formation of coexisting pair, nesquehonite – bar-ringtonite, was generated at the temperature 50°C on the expense of chrysotile after reactions 6. This pair is possible to clarify by reaction activity in the source metaperidotite (olivine, enstatite and diopside) from which the chrysotile was formed.

7.5 Minerals of artificial carbonatization formed at temperature 160 °C

A suspension of serpentine group minerals with CO_2 and H_2O was prepared from the source metaperidotite. This suspension was the source liquid from which after filtration and reaction under temperature regime 160°C a spherical form of hydromagnesite and globular clumps mixture of dypingite and hydromagnesite have been formed and locally the size of crystals reached nearly $100\text{ }\mu\text{m}$ (Fig. 7.4). Original grains of Ca-Mg silicate (chrysotile, enstatite, diopside) were replaced by the mixture of dypingite, magnesite and dolomite. During the process of carbonatization rare allotriomorphic grains of dolomite and magnesite were formed reaching the size of $7\text{ }\mu\text{m}$ (Fig. 7.4c). Original diopside was in the course of carbonatization hydrated and replaced by hydromagnesite (Fig. 7.4d).

The chemical formula of hydromagnesite is: $(\text{K}_{0.002}\text{Na}_{0.003}\text{Si}_{0.076}\text{Fe}_{0.002}\text{Mn}_{0.005}\text{Cr}_{0.007}\text{Ca}_{0.041}\text{Mg}_{4.861})_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$; dypingite $(\text{K}_{0.006}\text{Na}_{0.016}\text{Si}_{0.021}\text{Mn}_{0.004}\text{Fe}_{0.002}\text{Cr}_{0.053}\text{Ca}_{0.068}\text{Mg}_{4.832})_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$; dolomite $\text{Ca}_{0.39}\text{Mg}_{0.61}\text{CO}_3$; magnesite $\text{Ca}_{0.01}\text{Mg}_{0.99}\text{CO}_3$ and calcite $\text{Ca}_{0.97}\text{Mg}_{0.03}\text{CO}_3$ (Fig. 7.6. Tab. 7.2 and 7.3). In hydromagnesite the Cr_2O_3 content ranges from 0.11 wt. % to 1.85% and in dypingite from 1.02% to 1.54%. The presence of Cr_2O_3 in hydromagnesite and dypingite indicates a bond of Cr as the molecule of stichtite that formed the acid carbonates as well. The Cr_2O_3 content was not determined in magnesite, dolomite and calcite (Fig. 7.10).

The new assemblage of hydromagnesite, magnesite, dolomite and calcite is the final product of the reaction 7 where the serpentinite (chrysotile), diopside, and olivine reacted with H_2O and CO_2 . This reaction was derived from the equation between the main consumed minerals and new formed minerals taking notice of exact relation between cations and anions balance in the chemical formulas of minerals (Tables 7.2 and 7.3). The small content of elements was neglected in the chemical formula.

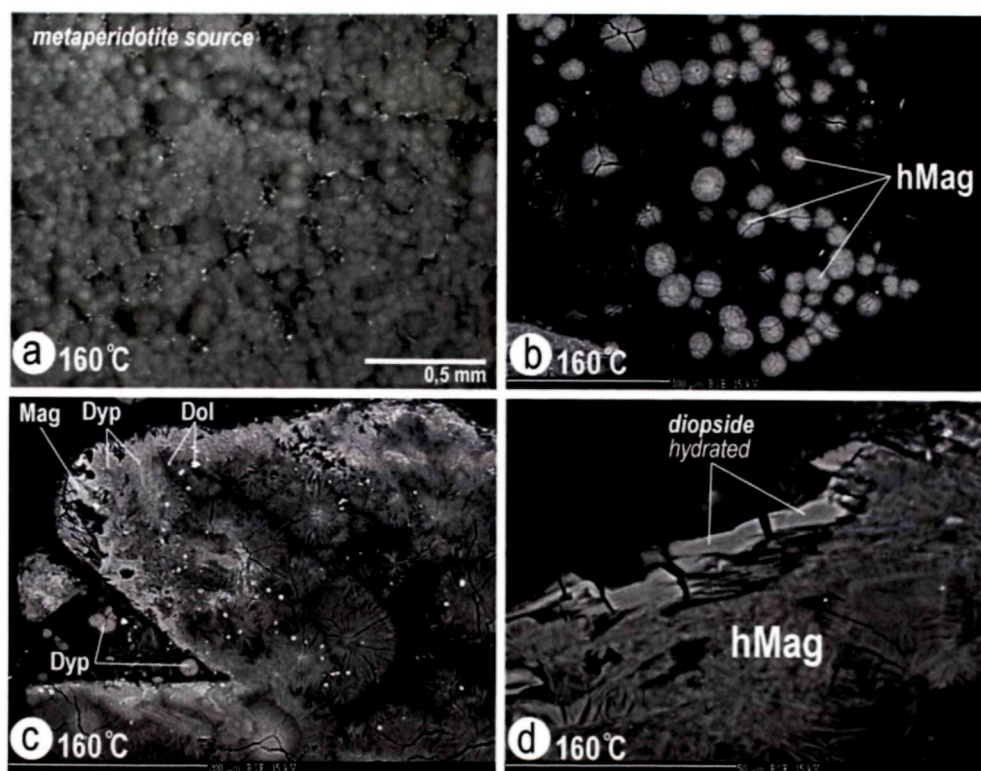
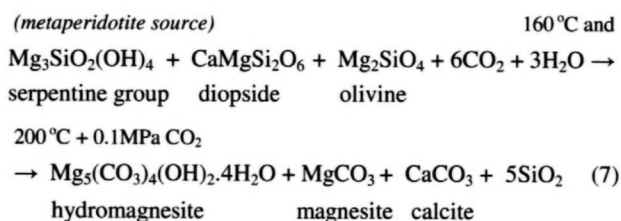


Fig. 7.4. Products of the artificial carbonatization were formed at temperature 160°C from the metaperidotite - serpentinite source. Sample HO-2 a) hydromagnesite (hMag) in binocular loupe, b) hydromagnesite in back-scattered electron image, c) relic of enstatite replaced by magnesite (Mag), dypingite (Dyp) and dolomite (Dol). Back-scattered electron image, d) relic of hydrated diopside replaced by hydromagnesite. Back-scattered electron image.

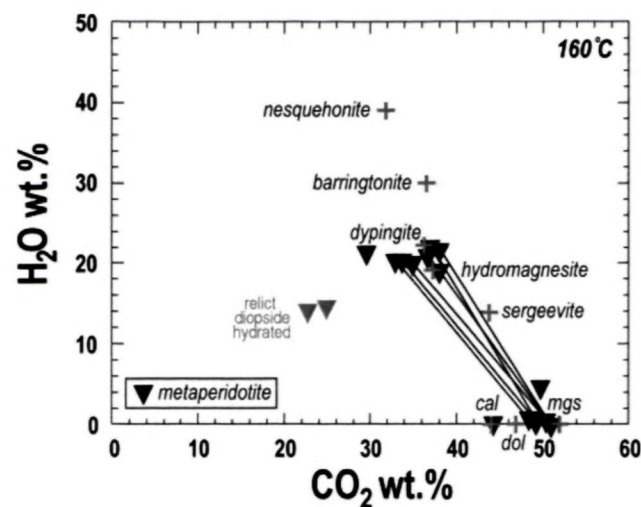


Fig. 7.5. Contents of H₂O and CO₂ in coexisting dypingite, hydromagnesite, calcite, dolomite and magnesite. Sample HO-2. These minerals were formed from the suspension (serpentinite + CO₂ + H₂O) during artificial carbonatization at temperature 160°C and from the metaperidotite source. Grey plus - contents of H₂O and CO₂ in end member minerals: cal - calcite, dol - dolomite, mag - magnesite. Grey reverse triangle - content of H₂O and CO₂ in hydrated relic of diopside.

7.6 Minerals of artificial carbonatization formed at temperature 200 °C

Analogically to previous case, also in this experiment was used the temperature at 200 °C. The acid carbonate of the spherical form and the irregular aggregates of magnesite, hydromagnesite and Ca magnesite crystallized

Table 7.2. Representative analyses of acid carbonates formed during artificial carbonatization under temperatures 160 and 200 °C. Neq-nesquehonite, Bar - barringtonite, Dyp - dypingite, Ser - sergeevite, hMag - hydromagnesite.

Sample	HO-2	HO-2	HO-2	HO-1	HO-2	HO-2	HO-2	HO-2
Mineral	Dyp	hMag	hMag	Dyp	Ser	hMag	Neq	Bar
Rock	peridotite	peridotite	peridotite	peridotite	peridotite	peridotite	peridotite	peridotite
Temper.	160°C	160°C	160°C	200°C	200°C	200°C	200°C	200°C
SiO ₂	0.25	0.95	0.97	1.63	0.34	0.88	0.56	0.64
TiO ₂	0	0	0	0	0	0	0	0
Al ₂ O ₃	0	0.01	0	0.01	0.02	0.02	0.02	0.01
Cr ₂ O ₃	1.02	1.80	0.11	0.13	0.02	0.18	0.10	0.03
FeO	0.03	0	0.05	0.03	0.34	0.06	0.01	0
MnO	0.06	0.03	0.07	0.01	0	0	0	0
MgO	38.57	43.14	41.36	34.54	20.19	43.28	28.16	34.73
CaO	0.57	0.76	0.48	1.39	19.27	0.61	0.39	0.53
Na ₂ O	0.10	0.16	0.02	0.04	0.01	0.02	0.02	0.04
K ₂ O	0.06	0.10	0.02	0.01	0	0	0.01	0.02
Cl	0.10	0.27	0.26	0.05	0.13	0.26	0.11	0.10
H ₂ O*	21.22	19.89	18.67	19.23	11.73	19.46	38.51	31.60
Total	61.98	67.11	62.01	57.07	52.05	64.77	67.89	67.70
CO ₂ *	38.02	32.89	37.99	42.93	47.05	35.23	32.11	32.30
Total *	100	100	100	100	100	100	100	100
O	11	10	10	11	23	10	4	3
Si	0.021	0.07	0.076	0.149	0.086	0.066	0.013	0.012
Al	0	0.01	0	0.001	0.006	0.002	0.001	0
Ti	0	0	0	0	0	0	0	0
Cr	0.068	0.105	0.007	0.009	0.004	0.011	0.002	0
Fe	0.002	0	0.003	0.002	0.072	0.004	0	0
Mg	4.832	4.729	4.861	4.694	7.607	4.874	0.975	0.976
Mn	0.004	0.002	0.005	0.001	0	0	0	0
Ca	0.051	0.060	0.041	0.136	5.218	0.049	0.010	0.011
Na	0.016	0.023	0.003	0.007	0	0.003	0.001	0.001
K	0.006	0.009	0.002	0.001	0.003	0	0	0
Total	5.000	4.999	4.998	5.000	12.996	5.009	1.002	1.000
CCl	0.028	0.067	0.070	0.015	0.111	0.067	0.009	0.006
OH	11.896	9.756	9.815	11.692	19.774	9.807	5.966	3.972

* calculated from chemical formula CO₂ * = 100 - Total *

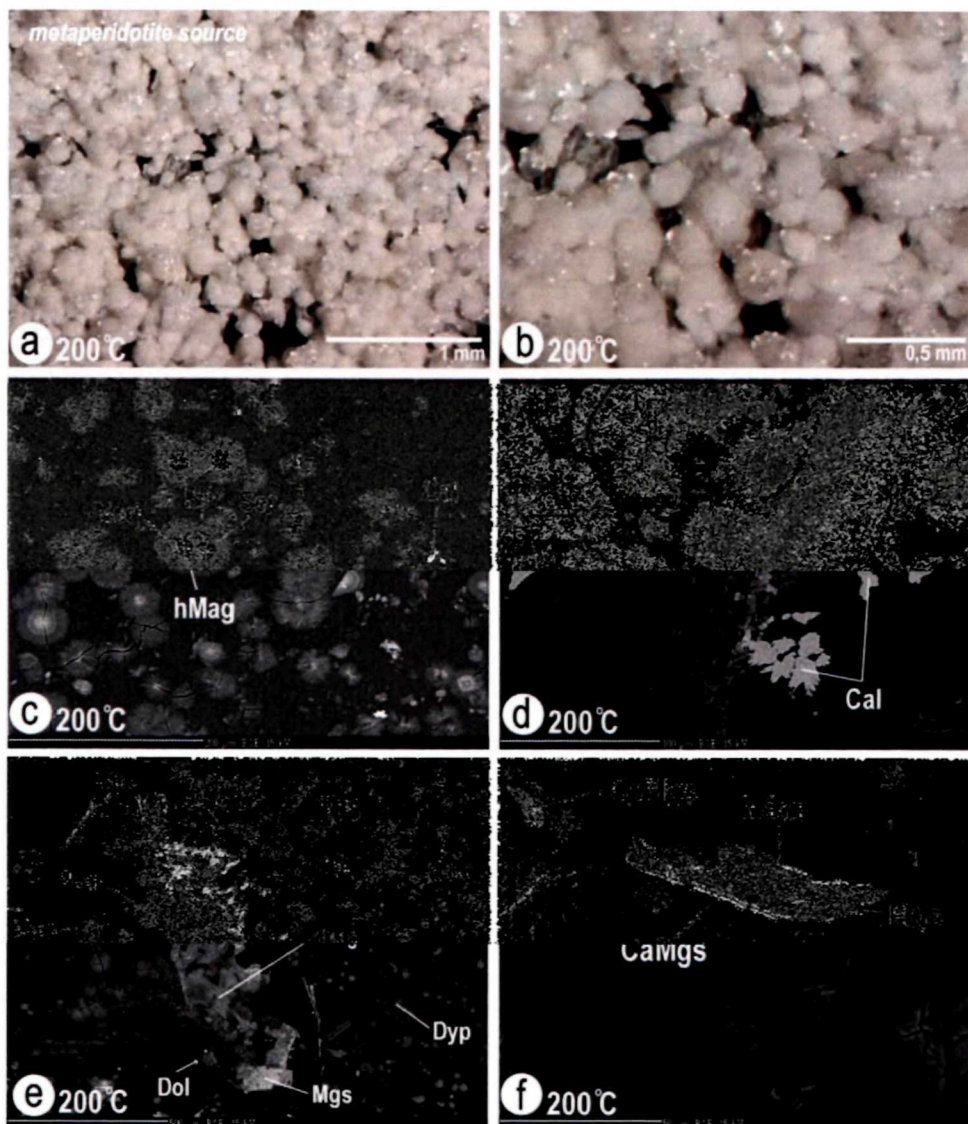


Fig. 7.6. Products of artificial carbonatization were formed at temperature 200 °C from the metaperidotite - serpentinite source. Sample HO-2, a) and b) spherical form of hydromagnesite (hMag), nesquehonite (Neq), barringtonite (Bar), sergeevite (Ser) and dypingite (Dyp) in binocular loupe, c) zonal grains of hydromagnesite (core), nesquehonite (rim), barringtonite (rim) and calcite (Cal). Back-scattered electron image, d) calcite and dypingite relation in back-scattered electron image, e) diopside replaced by calcite, by hydromagnesite, by dolomite (Dol) and magnesite (Mgs). Initial chrysotile (serpentine) was replaced by nesquehonite, hydromagnesite and dypingite. Back-scattered electron image, f) hydromagnesite, Ca magnesite (CaMgs) and magnesite in back-scattered electron image.

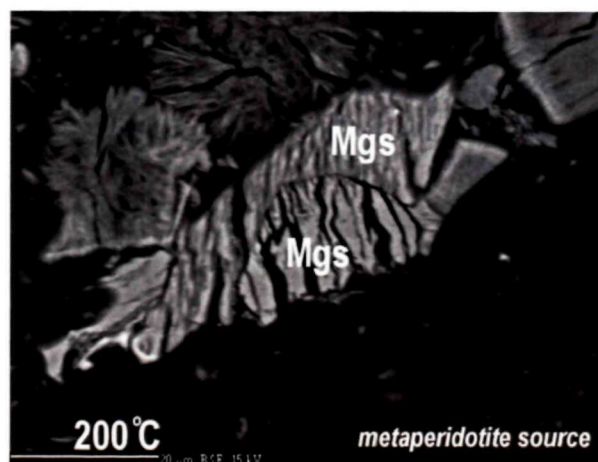


Fig. 7.7. Product of artificial carbonation was formed from metaperidotite source at the temperature of 200 °C. Sample HO-3; magnesite (Mgs) in back-scattered electron image.

Table 7.3. Representative analyses of carbonates formed during artificial carbonatization. Cal - calcite, Dol - dolomite, Mag - magnesite.

Sample	HO-2	HO-2	HO-2	HO-2	HO-2	RU-2	HO-2	HO-2	HO-2
Mineral	Cal	Dol	CaMag	Mag	Cal	Cal	Dol	CaMag	Mag
Rock	peridotite	peridotite	peridotite	peridotite	peridotite	websterite	peridotite	peridotite	peridotite
Temper.	160 °C	160 °C	160 °C	160 °C	200 °C	200 °C	200 °C	200 °C	200 °C
FeO	0	0	0.02	0	0	0.01	0.04	0	0
MnO	0.03	0	0	0.03	0.11	0.02	0	0.01	0.10
MgO	0.85	27.03	39.42	46.70	1.40	1.72	27.58	40.73	47.59
CaO	55.45	24.12	10.08	0.87	54.49	53.76	23.10	7.34	0.28
CO ₂ *	44.45	48.46	50.96	51.69	44.36	44.10	48.28	50.26	52.24
Total	100.78	99.61	100.48	99.29	100.36	99.61	99.00	98.34	100.21
O	3	6	3	3	3	3	6	3	3
Fe	0	0	0	0	0	0	0.002	0	0
Mn	0	0	0	0	0.002	0	0	0	0.001
Mg	0.021	1.218	0.845	0.987	0.034	0.043	1.248	0.885	0.995
Ca	0.979	0.782	0.155	0.013	0.964	0.957	0.750	0.115	0.004
Total	1.000	2.000	1.000	1.000	1.000	1.000	2.000	1.000	1.000

* calculated from chemical formula.

according to the reaction 7 from the source metaperidotite (Figs. 7.6 and 7.7). The spherical grains are zoned. The core form hydromagnesite, dypingite and/or sergeevite and the rim parts of rounded grains are formed by nesquehonite and/or barringtonite (Figs. 7.6c and 7.6e).

Hydromagnesite has almost identical values of X-ray diffraction profile and mineral lattice parameters as published in ASTM table values from the year 1974.

The chemical formula of nesquehonite is: $\text{Si}_{0.013}\text{Cr}_{0.002}\text{Ca}_{0.010}\text{Mg}_{0.975}(\text{HCO}_3)(\text{OH})\cdot 2\text{H}_2\text{O}$; barringtonite $\text{Na}_{0.001}\text{Ca}_{0.011}\text{Si}_{0.011}\text{Mg}_{0.976}\text{CO}_3\cdot 2\text{H}_2\text{O}$; dypingite $(\text{K}_{0.002}\text{Na}_{0.042}\text{Si}_{0.004}\text{Mn}_{0.002}\text{Cr}_{0.007}\text{Ca}_{0.033}\text{Mg}_{4.909})_5(\text{CO}_3)_4(\text{OH})_2\cdot 5\text{H}_2\text{O}$; hydromagnesite $(\text{K}_{0.002}\text{Si}_{0.001}\text{Mn}_{0.001}\text{Ca}_{0.007}\text{Mg}_{4.989})_5(\text{CO}_3)_4(\text{OH})_2\cdot 4\text{H}_2\text{O}$; sergeevite $(\text{K}_{0.006}\text{Na}_{0.013}\text{Si}_{0.458}\text{Mn}_{0.006}\text{Cr}_{0.025}\text{Al}_{0.003}\text{Fe}_{0.006}\text{Ca}_{1.845}\text{Mg}_{10.645})_{13}(\text{CO}_3)_9(\text{HCO}_3)_4(\text{OH})_4\cdot 6\text{H}_2\text{O}$; calcite $\text{Mg}_{0.03}\text{Ca}_{0.97}\text{CO}_3$; dolomite $\text{Mg}_{0.62}\text{Ca}_{0.38}\text{CO}_3$; Ca magnesite $\text{Mg}_{0.89}\text{Ca}_{0.12}\text{CO}_3$ and magnesite MgCO_3 (Figs. 7.9 and 7.10, Tables 7.2 and 7.3).

During artificial carbonatization controlled at the temperature 200 °C the new coexisting assemblage, hydromagnesite, magnesite, calcite and dolomite was formed from the metaperidotite source (Figs. 7.6 and 7.7). The same assemblage is the result of serpentine group and olivine reaction with the water and carbon dioxide which was formed at the temperature 160 °C according to the reaction 7.

7.7. Discussion

The reactions 6 and 7 have been evaluated by mass balance calculations based on the relation between the source rocks of mantle and their respondent minerals (serpentine group, olivine, enstatite, diopside) and $\text{CO}_2 + \text{H}_2\text{O}$ composition as well as according to new formed

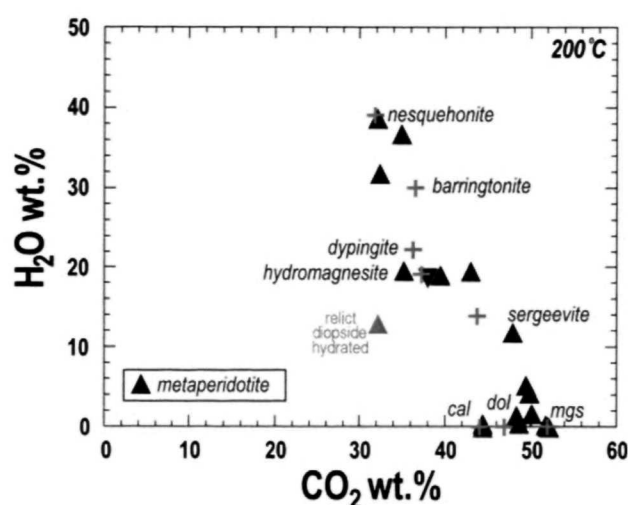


Fig. 7.8. Contents of H_2O and CO_2 in coexisting acid carbonates: nesquehonite, barringtonite, dypingite, hydromagnesite, sergeevite and carbonates: calcite, dolomite and magnesite. These minerals were formed from the suspension (serpentinite + $\text{CO}_2 + \text{H}_2\text{O}$) during artificial carbonatization at temperature 200 °C and from the metaperidotite source (sample HO-2 and HO-3). Grey plus - H_2O and CO_2 contents in end member minerals: cal - calcite, dol - dolomite, mgs - magnesite. Grey triangle - H_2O and CO_2 content in hydrated diopside.

acid carbonates and carbonates. These reactions represent the artificial carbonatization process, which can take place under various temperature conditions. A mass of carbon dioxide (kg) was calculated according to the mass balance of these reactions. Consequently, it allows to assess the mass of CO_2 consumed in 1 m³ of metaperidotite during artificial carbonatization process. In the course of reaction 6 controlled by temperature 50 °C it is possible to consume 1429 kg of CO_2 in 1 m³ of metaperidotite, pro-

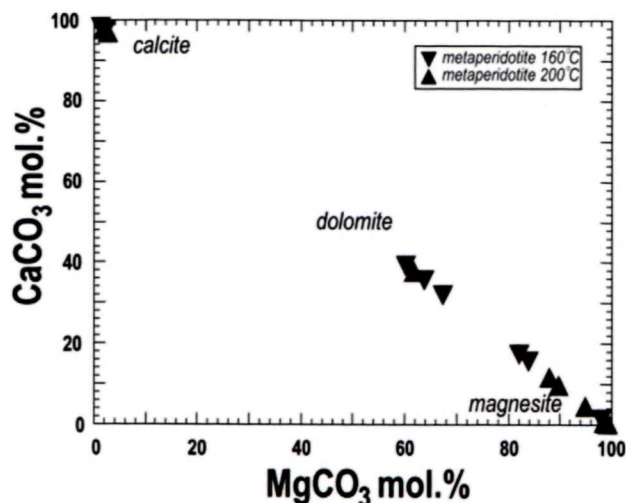


Fig. 7.9. Contents of CaCO₃ and MgCO₃ in carbonates. These minerals crystallized at the expense of silicates in metaperidotite.

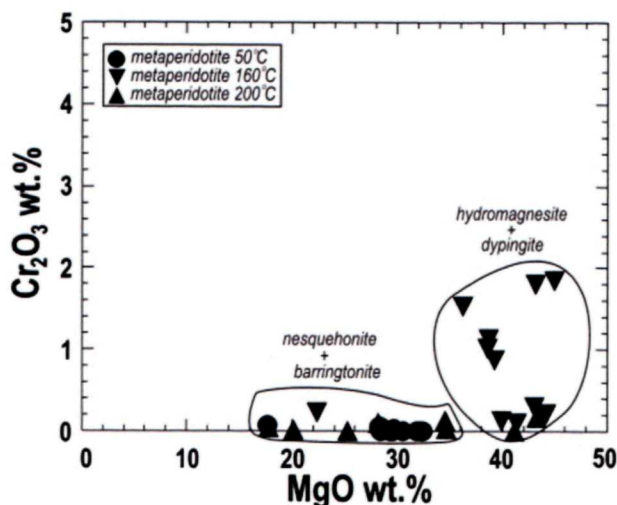


Fig. 7.10. Contents of Cr₂O₃ and MgO in nesquehonite, barringtonite, dypingite and hydromagnesite. Cr₂O₃ indicates presence of stichtite molecule Mg₆Cr₂(OH)₁₆(CO₃)₄·4(H₂O) in these minerals.

vided the volume density of metaperidotite is 3.0 kg·m⁻³. The capability of rock decreases to 1,224 kg of sequestered CO₂ in the case of lower volume density 2.57 kg·m⁻³ that is the value typical for serpentinite (Fig. 7.11).

The peridotite carbonatization process in conformity with the reaction 7 at temperature 160 °C as well as 200 °C consumes 1,249 kg of CO₂, alternatively, 1,070 kg of CO₂ in 1 m³ of rock in dependence on minimum, or maximum substance of serpentine group in metaperidotite. The results obtained from our investigation are in a very good agreement with comparative investigation and calculation (Herzog, 2002).

In comparison to ideal weight of CO₂ eliminated in 1 m³ of metaperidotite the consumed mass of carbon dioxide ranges from 1,070 kg to 1,429 kg and does not depend neither on temperature condition of artificial carbonatization nor the type of the source serpentinite. Gradual temperature increase from 50 °C through 160 °C to

200 °C has influence on higher participation of carbonates (calcite, dolomite, magnesite) at the expense of acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite). Acid carbonates preferably grow at temperature 50 °C while higher temperatures serve as a suitable environment for carbonates formation.

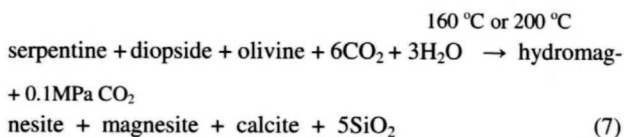
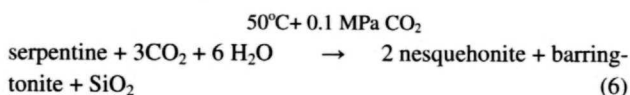


Fig. 7.11. Scheme of the volume of sequestered CO₂ in 1 m³ of metaperidotite.

7.8. Conclusion

The capability of metaperidotite (locality Hodkovce) to eliminate industrial CO₂ emissions has been verified by the experimental study of artificial carbonatization. Laboratory tests have been carried out on prepared samples of ultramafic rocks from above mentioned locality. The serpentinite was mixed with water at the temperature 22 °C, when the pressure of carbon dioxide was changed from 0.1 to 0.3 MPa and the time from 5 to 20 hours during reactions. The acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite), as well as carbonates (calcite, dolomite, and magnesite) crystallized from filtrate with pH value of about 8, during 4-24 hours (in dependency on the varying temperatures).

This group of new minerals crystallized according to the following reactions:



The reactions 6 and 7 served as the base for CO₂ weight calculation that resulted in the final conclusion - how many kg of carbon dioxide is capable 1 m³ of serpentinite to bond in its volume, under different temperature regimes. In comparison of ideal mass of CO₂ liquified in 1 m³ of metaperidotite, the sequestered mass of the carbon dioxide from 1,070 kg to 1,429 kg does not depend neither on the temperature condition of artificial carbonatization nor on the type of the source rock. The gradual temperature increase from 50 °C through 160 °C to 200 °C has influence on higher share of carbonates formation (calcite, dolomite, and magnesite) at the ex-

pense of acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite). Acid carbonates are dominating below temperature 50 °C while higher temperatures serve as a suitable environment for carbonates formation.

Results of experimental study show that serpentinite rocks are a suitable eliminator of CO₂ especially in the eastern part of Slovakia. Achieved results represent a solid base for better understanding the artificial carbonatization.