

# Permanent disposal of CO<sub>2</sub> industrial emission via artificial carbonatization of metaperidotite, metawehrlite and metawebsterite: an experimental study

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**Abstract.** The paper extends an experimental base for possibility to store the carbon dioxide emission via artificial carbonatization of metaperidotite bodies located in the East Slovakia. Three types of hydrated mantle rocks, metaperidotite (metaherzolitite), metawehrlite and metawebsterite were subjected to reaction with water and CO<sub>2</sub> and therefrom obtained suspensions were heated by the different temperatures of 50°C, 160 °C and 200 °C in the laboratory conditions. From the heated suspensions the acid carbonates (nesquehonite, barringtonite, dypingyte, 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 amount from 902 to 1264 kg of CO<sub>2</sub> can be sequestered in 1 m<sup>3</sup> of the source metaperidotite, metawehrlite and metawebsterite.

**Key words:** CO<sub>2</sub> disposal, artificial carbonatization, acid carbonates, carbonates, CO<sub>2</sub> storage capacity, metaperidotite, serpentinite

## 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 inside of the Earth. Nowadays it is estimated that its 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 risks and it demands an urgent global response. The methods to remove the anthropogenous carbon dioxide is a sequestration, understood as catching or separation, transport and storage of the CO<sub>2</sub> emission in the deep geological structures. CO<sub>2</sub> 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 blowing to the atmosphere, while the monitoring of CO<sub>2</sub> leakages from the CO<sub>2</sub> stored deposit has to be continuous.

- chemical – by mineral carbonation (“mineral sequestration”), consisting in binding CO<sub>2</sub> with minerals.

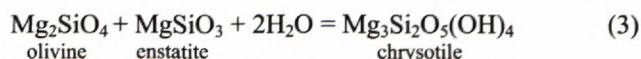
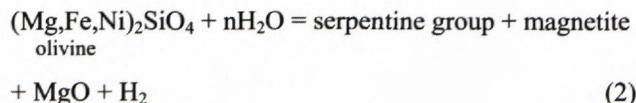
The mineral CO<sub>2</sub> sequestration is not so preferred in comparison to deposition in regional aquifers, or depleted hydrocarbon deposits. However it is concerned to be one of the approaches which can be helpful in the combat climate change (Schiller, 2006; Uibu, 2008).

Serpentinite has been proposed as an efficient reagent for CO<sub>2</sub> sequestration by reason that the highly magnesian serpentinite or forsteritic olivine favors 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, dypingyte 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).

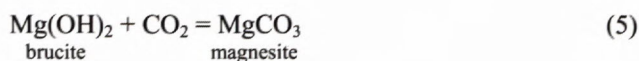
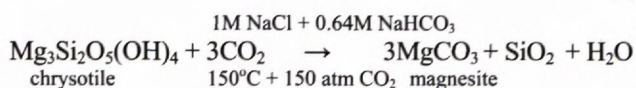
Serpentinite forms by hydration of olivine and enstatite at variable depths in the Earth's crust or mantle during regional metamorphism. Alternatively, it can be formed by water alternation on the surface in conformity with reactions 1, 2, and 3 (Johannes, 1968; Martin & Fyfe, 1970; Malakhov, 1971):







According to the exchange reactions 4 and 5 the serpentine group (chrysotile) reacts with  $\text{CO}_2$  to produce magnesite during its carbonatization in atmosphere conditions (Herzog, 2002, Drobek et al., 2008). However a process of artificial carbonatization uses  $\text{NaCl}$  and  $\text{NaHCO}_3$  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 tone of  $\text{CO}_2$  is necessary to utilize rock weight from 2.1 to 3.18 tons 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  $\text{CO}_2$  storage. Those bodies which were not influenced by natural  $\text{CO}_2$  during metamorphism, or exhumation, are suitable for the artificial carbonatization purposes. Therefore a mineralogical and petrological study of the bodies is needed, because its 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 on localities 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 by variable content of carbonate finds (Hovorka et al., 1985). It means that their evaluation for account of carbon dioxide sequestration requests detailed mineralogical and petrological study. However this is not the only criteria for usable serpentinite body, but its volume, depth, morphology and tectonic structure are important too.

A dominant  $\text{CO}_2$  producer in Slovakia is US STEEL Ltd. with annual production more than 11 Mtons per year. Due to fact, that surrounding of this plant from geological point of view are suitable for  $\text{CO}_2$  storage by various methods. The area near the producer is aimed at the largest ultramafic body of metaperidotite, with extension about several  $\text{km}^3$ . The outcrop of metaperidotite is located near Hodkovce. In addition besides of the Komárovce – Hodkovce large body, there is located small

metawebsterite body near Rudník and the metawehrlite body near Jasov, both have several  $100 \text{ m}^3$  in size (Zlocha, 1980). Encouraging of body circumstances in the depth is confirmed by a high temperature gradient in Komárovce – Hodkovce metaperidoite body because the reactions 4 and 5 which transform serpentinite to carbonates have an optimum temperature interval from 70 to  $130^\circ\text{C}$ . Such a temperature  $59^\circ\text{C}$  has been measured in the depth below 1500 m in the borehole KO-1 near Komárovce (Biela, 1978; Franko et al., 1995).

The aim of this study is test of mantle rocks capability (metaperidotite, metawehrlite, metawebsterite), selected from the East Slovakian area for permanent carbon dioxide liquidation by artificial carbonatization. A consistent bonding of  $\text{CO}_2$  in crystal lattice of carbonates is sustained and ecological solution for  $\text{CO}_2$  mitigation purposes (Goldberg et al., 2000; Herzog, 2002; Kelemen & Matter, 2008).

## 2. Mineral composition of source mantle rocks

The serpentinitized mantle-derived rocks were studied at localities Hodkovce (HO-1 and HO-2, metaperidotite), Rudník (RU-1 and RU-2, metawebsterite) and Jasov (JA-1 metawehrlite). The minerals of serpentine group are prevailing over the former magmatic mineral association (olivine and pyroxenes). Therefore it is possible to classify all studied rocks 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 %). The content of Cr-spinel is in the both samples less than 0.5 %. Moreover, it is possible to recognize hornblende, hornblende – pargasite, tremolite, Ni sulphides and talc in accessory quantity.

**Metawebsterite** is formed by antigorite + chrysotile (68 vol. %, or 77 %), Al-enstatite + Al-dioside ± fayalite (20 %, or 13 %), magnetite prevails over oxide mineral association: pyrophanite + Mn-rutile + Cr-magnetite (together 5 %); calcite (7.9 % or 3.6 %). Content of Al-spinel in both samples is below 0.5 %. Following minerals can be found in accessory concentrations: pargasite + millerite + Si-mineral (quartz?) + melanite + Cr-garnet + schwaningite + chlorite + cronstedtite – kellyite + Ba-asbolane (?) + Co-Mn mineral (?) + andradite + diabanite and barite.

**Metawehrlite** is composed of lizardite + chrysotile + antigorite + Ni-Fe serpentine (79 vol. %). Ti-diopside + Na-diopside + diopside ± olivine (8 %); magnetite + Cr-magnetite + hematite + Cr-hematite + Mn-hematite (together 7 %) dominates over oxide and carbonate association: rutile + calcite + Cr-spinel (6 %). This rock sporadically contains millerite + siegenite + melanite + grosular + andradite + ermenickelite + Cr-chlorite.

## 3. Sample preparation and analytical conditions

Polished thin sections of source metaperidotite, metawehrlite and metawebsterite were studied under polarizing microscope. We have focused on 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 at State Geological Institute of Dionýz Štúr, Bratislava. Microprobe was operated with accelerating voltage 15 KV, sample current 5-20 nA and the size of beam diameter varied from 5 to 20 µm in relation to the measured mineral. The counting time was 10 s and for fluorine 25 s. The following calibration standards were used: Ca-wolastonite, Mn-rhodonite, Na-albite, K-orthoclase and Cr-chromite., Ti-TiO<sub>2</sub>, Al-Al<sub>2</sub>O<sub>3</sub>, Fe-fayalite, Mg-MgO and F-BaF<sub>2</sub>. Detecting limit for individual elements was less than 0.05 wt. % with mistake 1 σ.

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 at State Geological Institute of Dionýz Štúr, Košice and silicate analyses were obtained by differential termogravity analyses (Tuček et al., 2009).

Experimental study has been conducted at such dressed samples. Serpentinite was mixed with water and carbon dioxide according to the procedure used by Tuček et al., (2009). Stable temperature, 22 °C and CO<sub>2</sub> pressure from 0.1 to 0.3 MPa was maintained during controlled reaction from 5 to 20 hours. Leaches, with pH value about 8 become 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 the optical methods and were analysed and controlled by electron microprobe, by CHA (chemical silicate analyses) RTG (X-ray diffraction analyses), by DTA (differential thermic analyses) and by DTG (differential thermogravimetric analyses) where the almost end-member of acid carbonates and carbonates have been found.

The photos of artificial carbonatization products have been 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 analyses.

#### 4. 1 Minerals of artificial carbonatization formed at temperature 50 °C

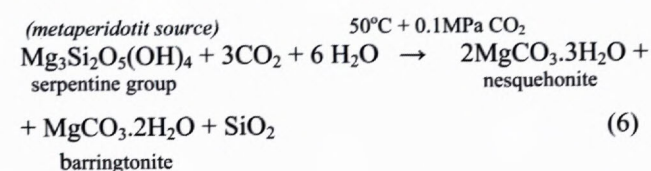
A homogeneous, idiomorphic nesquehonite or aggregations of nesquehonite and barringtonite up to size almost 1 mm were upraised from the suspension (serpentinite + CO<sub>2</sub> + H<sub>2</sub>O) after reaction, filtration and crystallization from the filtrate (Fig. 2). Original source rock - metaperidotite was during experiment under constant temperature of 50 °C. A mixture of radial or omnidirectional aligned nesquehonite was formed from the original metawehrlite. The nesquehonite is sporadically fibrillated by a hemisphere of dypingite, and hydromagnesite (Fig. 4). The original calcite, which was formed in metawehrlite during its serpentinisation, was in time nesquehonite and dypingyte formation hydrated, while original dolomite remained stable without its chemical composition changes (Fig. 4d).

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

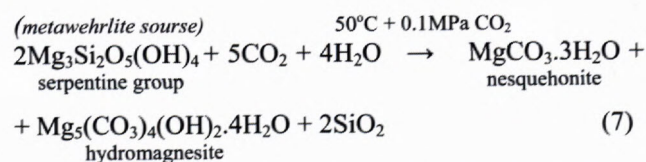
The chemical formula of nesquehonite is Si<sub>0.001</sub>Fe<sub>0.001</sub>Cr<sub>0.001</sub>Ca<sub>0.002</sub>Mg<sub>0.995</sub>(HCO<sub>3</sub>)(OH).2H<sub>2</sub>O; barringtonite K<sub>0.001</sub>Ca<sub>0.001</sub>Mg<sub>0.999</sub>CO<sub>3</sub>.2H<sub>2</sub>O; dypingite K<sub>0.003</sub>Na<sub>0.008</sub>Si<sub>0.061</sub>Al<sub>0.016</sub>Fe<sub>0.03</sub>Cr<sub>0.053</sub>Ca<sub>0.090</sub>Mg<sub>4.765</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>.5H<sub>2</sub>O and hydromagnesite (K<sub>0.003</sub>Na<sub>0.003</sub>Si<sub>0.099</sub>Al<sub>0.012</sub>Fe<sub>0.005</sub>Cr<sub>0.025</sub>Ca<sub>0.083</sub>Mg<sub>4.772</sub>)<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>.4H<sub>2</sub>O (Fig. 5, Tab. 2).

In hydromagnesite and dypingite the Cr<sub>2</sub>O<sub>3</sub> content ranges from 0.41 wt. % to 1.42 % and the highest content of Cr<sub>2</sub>O<sub>3</sub> in nesquehonite reaches 0.11 % (Fig. 12). The variable content of Cr<sub>2</sub>O<sub>3</sub> indicates a bond of Cr as the stichtite molecule in hydromagnesite and dypingite.

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 (Fig. 5). 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. 1). Low element contents were omitted in chemical formulas.



The coexisting mixture of nesquehonite and hydromagnesite was formed after the reaction of chrysotile with water and carbon dioxide. The mixture of acid carbonates formed from the metawehrlite-matrix was in conformity with reaction 7 by the same temperature of 50 °C (Fig. 5). The set up and procedure of the reaction 7 was identical as in the previous case (6).



The formation of two different coexisting pairs, nesquehonite – barringtonite and nesquehonite – hydromagnesite were formed at the same temperature 50 °C on the expense of chrysotile after reactions 6 and 7. Two different pairs are possible to clarify by different reaction activity in the source metaperidotite and metawehrlite from which the chrysotile was formed. Olivine, enstatite and diopside replaced by chrysotile during metamorphism or hydration of peridotite have probably different reaction ability (activity) than from the chemical point of view identical to chrysotile which was formed in metawehrlite by the hydration of diopside. In conformity with juxtaposition of reactions 6 and 7, metawehrlite consumes less amount of CO<sub>2</sub> during artificial carbonatization than metaperidotite.



Tab. 1 Representative analyses of acid carbonates formed during artificial carbonatization by temperature 50 °C. Neq-nesquehonite, Bar-barringtonite, Dyp-dypingite, hMag-hydromagnesite.

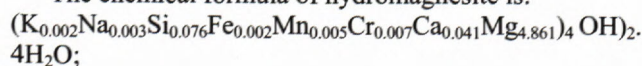
Sample Mineral Rock Temper.	HO-1 Neq peridotite 50 °C	HO-1 CaNeq peridotite 50 °C	HO-2 Neq peridotite 50 °C	HO-1 Bar peridotite 50 °C	HO-2 Bar peridotite 50 °C	JA-1 Neq wehrlite 50 °C	JA-1 Neq wehrlite 50 °C	JA-1 Dyp wehrlite 50 °C	JA-1 hMag wehrlite 50 °C
SiO <sub>2</sub>	0.06	0.29	0.09	0	0.02	0	0	0.82	1.26
TiO <sub>2</sub>	0	0	0	0	0	0	0	0	0
Al <sub>2</sub> O <sub>3</sub>	0	0.09	0	0	0	0	0.05	0	0.13
Cr <sub>2</sub> O <sub>3</sub>	0.06	0.08	0.03	0	0	0.11	0	0.54	0.41
FeO	0	0.03	0.07	0	0.02	0.60	0	0.02	0.08
MnO	0	0	0.02	0	0.01	0	0	0.03	0.02
MgO	28.33	17.63	29.59	32.48	32.18	27.40	29.80	35.33	40.69
CaO	0.03	17.11	0.04	0.04	0	0.09	0.05	0.56	0.99
Na <sub>2</sub> O	0	0.06	0	0	0.04	0	0	0.09	0.02
K <sub>2</sub> O	0	0.01	0	0.04	0	0	0.02	0.03	0.03
Cl	0	0.08	0	0	0	0	0.02	0.61	0.84
H <sub>2</sub> O*	38.20	40.67	39.98	29.08	28.83	37.40	40.10	19.27	18.38
Total	66.69	76.05	69.82	61.64	61.10	65.60	70.04	57.30	62.85
CO <sub>2</sub> *	33.31	23.95	30.18	38.36	38.90	34.40	29.96	42.70	37.15
Total *	100	100	100	100	100	100	100	100	100
O	4	4	4	3	3	4	4	11	10
Si	0.001	0.006	0.002	0	0	0	0	0.075	0.099
Al	0	0.002	0	0	0	0	0.001	0	0.012
Ti	0	0	0	0	0	0	0	0	0
Cr	0.001	0.001	0.001	0	0	0.002	0	0.039	0.025
Fe	0	0.001	0.001	0	0	0.012	0	0.002	0.005
Mg	0.995	0.580	0.992	0.999	0.998	0.982	0.997	4.808	4.772
Mn	0	0	0	0	0	0.002	0	0.002	0.001
Ca	0.001	0.405	0.001	0.001	0	0	0.001	0.055	0.083
Na	0	0.001	0	0	0.002	0	0	0.016	0.003
K	0	0	0	0.001	0	0	0.001	0.003	0.003
Total	0.998	0.998	0.997	1.001	1.000	0.998	1.000	5.000	5.003
CCl	0	0.006	0	0	0	0	0.002	0.189	0.224
OH	6	5.987	6	4	4	6	5.999	11.736	9.648

\* calculated from chemical formula, CO<sub>2</sub> = 100 – Total \*

#### 4.2 Minerals of artificial carbonatization formed at temperature 160 °C

A suspension of serpentine group minerals with CO<sub>2</sub> and H<sub>2</sub>O 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 has been formed and locally the size of crystals reach nearly 100 μm (Fig. 5). Original grains of Ca–Mg silicate (chrysotile, enstatite, diopside) were replaced by the mixture of dypingite, magnesite and dolomite. During the process of carbonatization the rare and allotriomorphic grains of dolomite and magnesite were formed reaching the size of 7 μm (Fig. 5c). Original diopside was in the course of carbonatization hydrated and replaced by hydromagnesite. (Fig. 5d)

The chemical formula of hydromagnesite is:



dypingite  $(K_{0.006}Na_{0.016}Si_{0.021}Mn_{0.004}Fe_{0.002}Cr_{0.053}Ca_{0.068}Mg_{4.832})_5(CO_3)_4(OH)_2 \cdot 5H_2O$ ; dolomite  $Ca_{0.39}Mg_{0.61}CO_3$ ; magnesite  $Ca_{0.01}Mg_{0.99}CO_3$  and calcite  $Ca_{0.97}Mg_{0.03}CO_3$  (Fig. 6., Tab. 3 and 4). In hydromagnesite the Cr<sub>2</sub>O<sub>3</sub> content ranges from 0.11 wt. % to 1.85 % and in dypingite ranges from 1.02 % to 1.54 %. The presence of Cr<sub>2</sub>O<sub>3</sub> in hydromagnesite and dypingite indicates a bond of Cr as the molecule of stichtite that was formed the acid carbonates as well. The Cr<sub>2</sub>O<sub>3</sub> content was not determined in magnesite, dolomite and calcite (Fig. 11).

The new assemblage of hydromagnesite, magnesite, dolomite and calcite is the final product of reaction 8 where the serpentinite (chrysotile), diopside, and olivine reacted with H<sub>2</sub>O and CO<sub>2</sub>. 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 3 and 4). The small content of elements was neglected in the chemical formula.





Tab. 2 Representative analyses of acid carbonates formed during artificial carbonatization by temperature 160 and 200 °C. Neq-mesquehonite, Bar-barringtonite, Dyp-dypingite, Ser-sergeevite, hMag-hydromagnezit.

Sample Mineral Rock Temper.	HO-2 Dyp peridotite 160°C	HO-2 hMag peridotite 160°C	HO-2 hMag peridotite 200°C	HO-2 Ser peridotite 200°C	HO-2 hMag peridotite 200°C	HO-2 Neq peridotite 200°C	HO-2 Bar peridotite 200°C	RU-1 Dyp webste. 200°C	RU-1 Ser webste. 200°C	RU-1 hMag webste. 200°C	RU-1 hMag webste. 200°C	RU-1 hMag webste. 200°C	RU-1 Neq webste. 200°C	RU-1 Bar webste. 200°C
SiO <sub>2</sub>	0.25	0.95	0.97	1.63	0.34	0.88	0.56	0.64	2.03	0.65	0.91	0.48	0.83	
TiO <sub>2</sub>	0	0	0	0	0	0	0	0	0	0	0	0	0	
Al <sub>2</sub> O <sub>3</sub>	0	0.01	0	0.01	0.02	0.02	0.02	0.01	0.01	0	0	0	0.01	
Cr <sub>2</sub> O <sub>3</sub>	1.02	1.80	0.11	0.13	0.02	0.18	0.10	0.03	0.14	0.16	4.16	0.78	0.09	
FeO	0.03	0	0.05	0.03	0.34	0.06	0.01	0	0.03	0	0	0	0	
MnO	0.06	0.03	0.07	0.01	0	0	0	0	0.02	0	0.04	0.02	0.01	
MgO	38.57	43.14	41.36	34.54	20.19	43.28	28.16	34.73	31.63	40.41	37.64	29.20	23.38	
CaO	0.57	0.76	0.48	1.39	19.27	0.61	0.39	0.53	7.63	1.22	0.63	0.35	7.98	
Na <sub>2</sub> O	0.10	0.16	0.02	0.04	0.01	0.02	0.02	0.04	0.03	0.09	0.04	0.21	0	
K <sub>2</sub> O	0.06	0.10	0.02	0.01	0	0	0.01	0.02	0.02	0.07	0.03	0.06	0.01	
Cl	0.10	0.27	0.26	0.05	0.13	0.26	0.11	0.10	0.04	0.08	0.58	0.55	0.03	
H <sub>2</sub> O*	21.22	19.89	18.67	19.23	11.73	19.46	38.51	31.60	12.66	18.55	17.43	40.48	26.34	
Total	61.98	67.11	62.01	57.07	52.05	64.77	67.89	67.70	54.25	61.23	61.46	72.14	58.68	
CO <sub>2</sub> *	38.02	32.89	37.99	42.93	47.05	35.23	32.11	32.30	45.75	38.77	38.54	27.86	41.32	
Total*	100	100	100	100	100	100	100	100	100	100	100	100	100	
O	11	10	10	11	23	10	4	3	23	10	10	4	3	
Si	0.021	0.07	0.076	0.149	0.086	0.066	0.013	0.012	0.458	0.052	0.074	0.011	0.019	
Al	0	0.01	0	0.001	0.006	0.002	0.001	0	0.003	0	0	0	0	
Ti	0	0	0	0	0	0	0	0	0	0	0	0	0	
Cr	0.068	0.105	0.007	0.009	0.004	0.011	0.002	0	0.025	0.010	0.29	0.014	0.002	
Fe	0.002	0	0.003	0.002	0.072	0.004	0	0	0.006	0	0	0	0	
Mg	4.832	4.729	4.861	4.694	7.607	4.874	0.975	0.976	10.642	4.816	4.590	0.959	0.786	
Min	0.004	0.002	0.005	0.001	0	0	0	0	0.006	0	0.003	0	0	
Ca	0.051	0.060	0.041	0.136	5.218	0.049	0.010	0.011	1.845	0.104	0.055	0.008	0.193	
Na	0.016	0.023	0.003	0.007	0	0.003	0.001	0.001	0.013	0.014	0.006	0.009	0	
K	0.006	0.009	0.002	0.001	0.003	0	0	0	0.006	0.007	0.003	0.002	0	
Total	5.000	4.999	4.998	5.000	12.996	5.009	1.002	1.000	13.004	5.003	5.000	1.003	1.000	
CCI	0.028	0.067	0.070	0.015	0.111	0.067	0.009	0.006	0.031	0.022	0.161	0.041	0.002	
OH	11.896	9.756	9.815	11.692	19.774	9.807	5.966	3.972	19.055	9.889	9.510	5.949	3.961	

\* calculated from chemical formula CO<sub>2</sub> \* = 100 - Total \*



Tab. 3 Representative analyses of carbonates formed during artificial carbonatization. Cal-kalcite, Dol-dolomite, Mag-magnesite.

Sample	Ja-1	HO-2	HO-2	HO-2	HO-2	HO-2	RU-2	HO-2	HO-2	HO-2
Mineral	Dol-relikt	Cal	Dol	CaMag	Mag	Cal	Cal	Dol	CaMag	Mag
Rock	wehrlite	peridotite	peridotite	peridotite	peridotite	peridotite	websterite	peridotite	peridotite	peridotite
Temper.	50 °C	160 °C	160 °C	160 °C	160 °C	200 °C	200 °C	200 °C	200 °C	200 °C
FeO	0.88	0	0	0.02	0	0	0.01	0.04	0	0
MnO	0.05	0.03	0	0	0.03	0.11	0.02	0	0.01	0.10
MgO	25.23	0.85	27.03	39.42	46.70	1.40	1.72	27.58	40.73	47.59
CaO	25.93	55.45	24.12	10.08	0.87	54.49	53.76	23.10	7.34	0.28
CO <sub>2</sub> *	48.46	44.45	48.46	50.96	51.69	44.36	44.10	48.28	50.26	52.24
Total	100.55	100.78	99.61	100.48	99.29	100.36	99.61	99.00	98.34	100.21
O	6	3	6	3	3	3	3	6	3	3
Fe	0.022	0	0	0	0	0	0	0.002	0	0
Mn	0.002	0	0	0	0	0.002	0	0	0	0.001
Mg	1.138	0.021	1.218	0.845	0.987	0.034	0.043	1.248	0.885	0.995
Ca	0.840	0.979	0.782	0.155	0.013	0.964	0.957	0.750	0.115	0.004
Total	2.002	1.000	2.000	1.000	1.000	1.000	1.000	2.000	1.000	1.000

\* calculated from chemical formula.

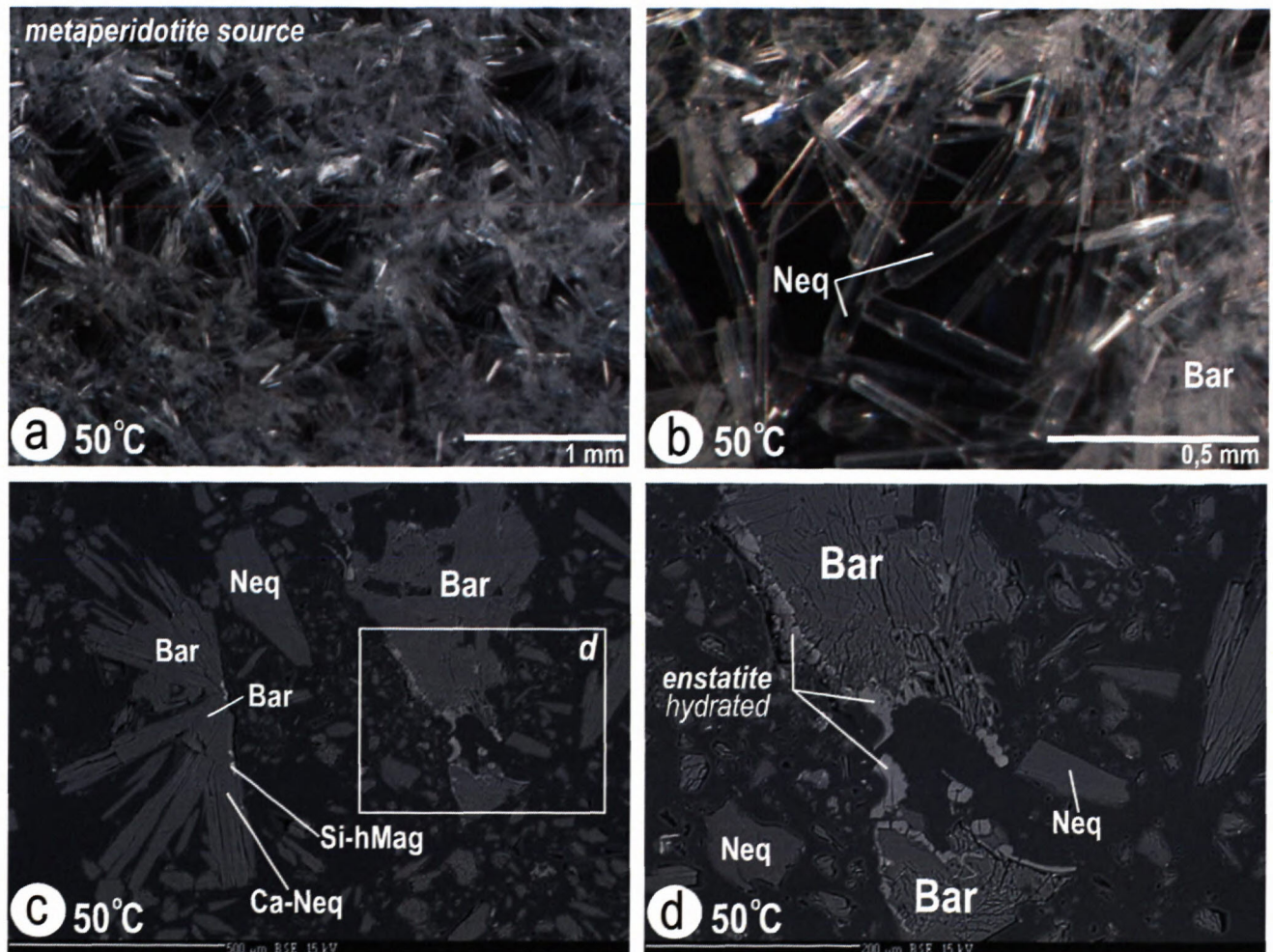


Fig. 1 Nesquehonite (Neq) and barringtonite (Bar) were formed during artificial carbonatization process at temperature 50 °C from the metaperidotite – serpentinite source. Sample HO-1., a) idiomorphic crystals of nesquehonite in binocular loupe, b) idiomorphic crystals of nesquehonite and barringtonite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



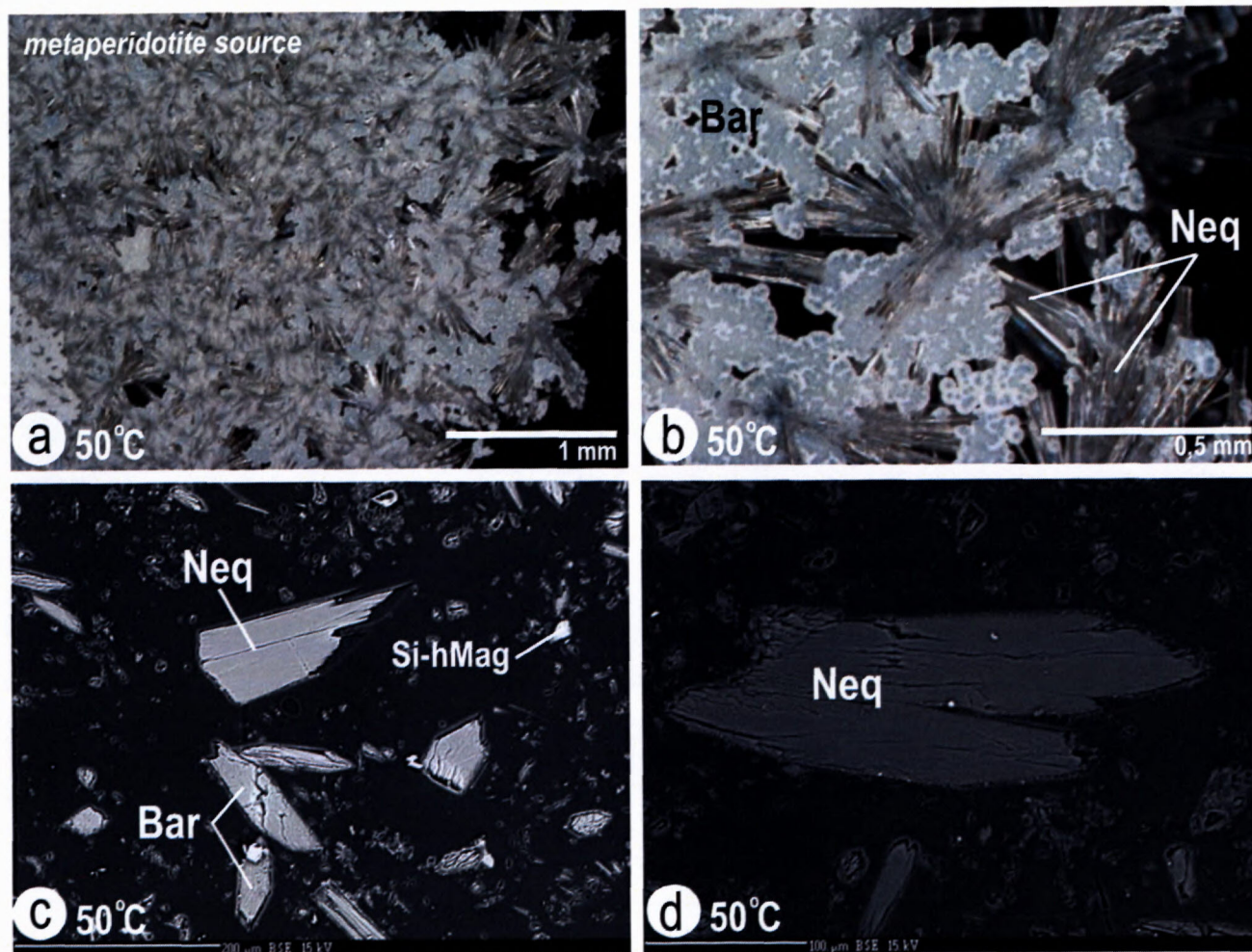


Fig. 2 Nesquehonite (Neq), barringtonite (Bar) and hydromagnesite (hMag) formed the artificial carbonatization process at temperature 50 °C from the metaperidotite – serpentinite source. Sample HO-2., a) nesquehonite and barringtonite in binocular loupe, b) nesquehonite and barringtonite in binocular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

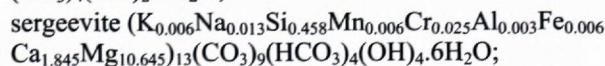
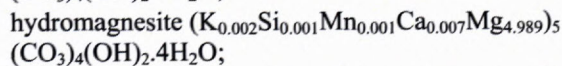
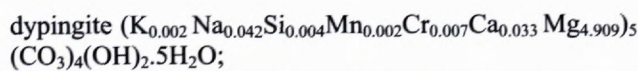
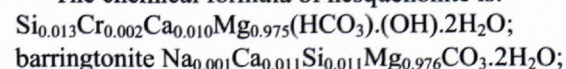
### 4.3 Minerals of artificial carbonatization formed at temperature 200 °C

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 according to reaction 8 from the source metaperidotite (Figs. 7 and 8d). The spherical grains are zoned. The core forms hydromagnesite, dypingite and/or sergeevite and the rim parts of rounded grains are formed by nesquehonite and barringtonite (Figs. 7c and 7e).

A new assemblage of Si nesquehonite, nesquehonite, hydromagnesite, dypingite and calcite crystallized from the source metabasite. The spherical form has sergeevite and barringtonite (Fig. 8).

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:



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  $\text{MgCO}_3$  (Figs. 9 and 10, Tables 3 and 4). In nesquehonite and hydromagnesite the Cr<sub>2</sub>O<sub>3</sub> content is ranging from 0.79 wt. % to 2.16 % with the sporadic value of 4.16 % (Fig. 11). In this acid carbonates, the Cr<sub>2</sub>O<sub>3</sub> content indicate the bond of Cr in the stichtite molecule.

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 and 8d). The same assemblage is the result of serpentine group and olivine reaction with the water and carbon dioxide which was formed by the temperature 160 °C according to the reaction 8.

Hydromagnesite, nesquehonite and calcite crystallized during the metabasite carbonatization where the



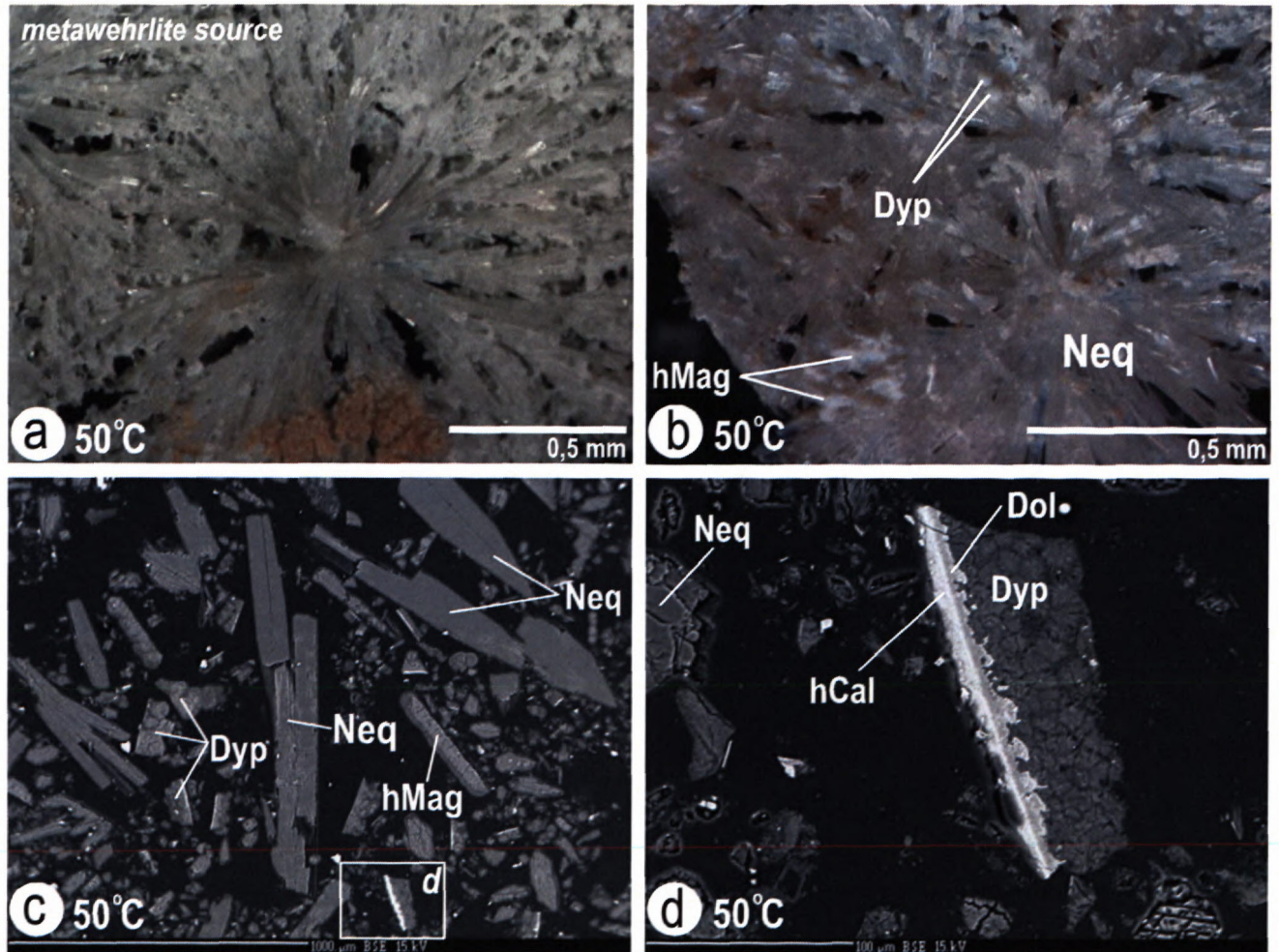


Fig. 3 Nesquehonite (Neq) and dypingite (Dyp) were formed during artificial carbonatization process at temperature 50 °C from the metawehrlite – serpentinite source. Sample JA-1., a) radial nesquehonite and dypingite in binocular loupe, b) nesquehonite and dypingite in binocular loupe, c) nesquehonite, dypingite and hydromagnesite (hMag). Back-scattered electron image., d) detail-c relict of hydrated calcite (hCal) and dolomite (Dol) replaced by dypingite and nesquehonite in back-scattered electron image.

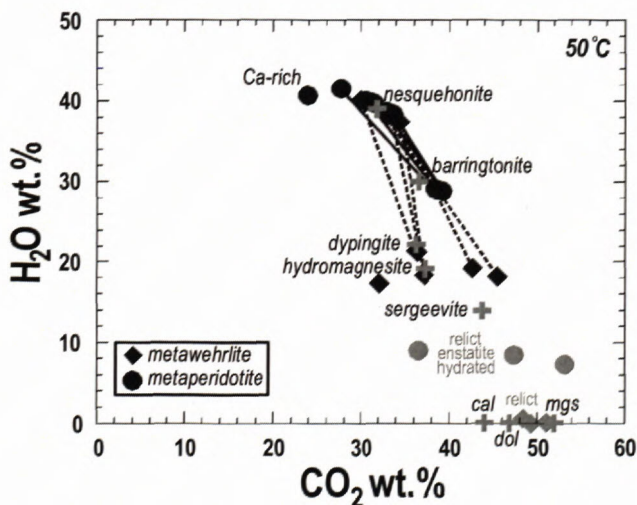
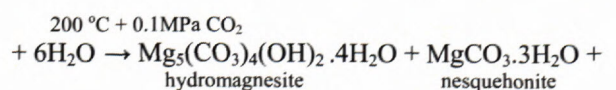
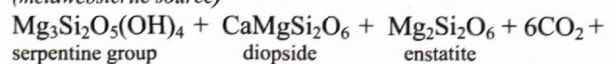


Fig. 4 Variation of H<sub>2</sub>O and CO<sub>2</sub> in coexisting pair of nesquehonite – barringtonite (sample HO-1 and HO-2 metaperidotite source) and in coexisting pair nesquehonite – dypingite/hydromagnesite (sample JA-1 metawehrlite source). These acid carbonates crystallized during artificial carbonatization controlled by temperature 50 °C. Grey plus – contents of H<sub>2</sub>O

and CO<sub>2</sub> in end member minerals: cal – calcite, dol – dolomite, mag – magnesite. Grey circles - contents of H<sub>2</sub>O and CO<sub>2</sub> in hydrated relict of enstatite. Grey rhomb – Carbonate relics from original metawehrlite.

temperature was 200 °C (Fig. 8). The carbonatization is result of the relation between main responsive minerals in metabeesterite to new formed minerals. It is driven by cations and anions balance in chemical formulas of minerals following reaction 9 (Tables 2 and 3). The small content of elements was omitted in the chemical formula.

(metawebsterite source)





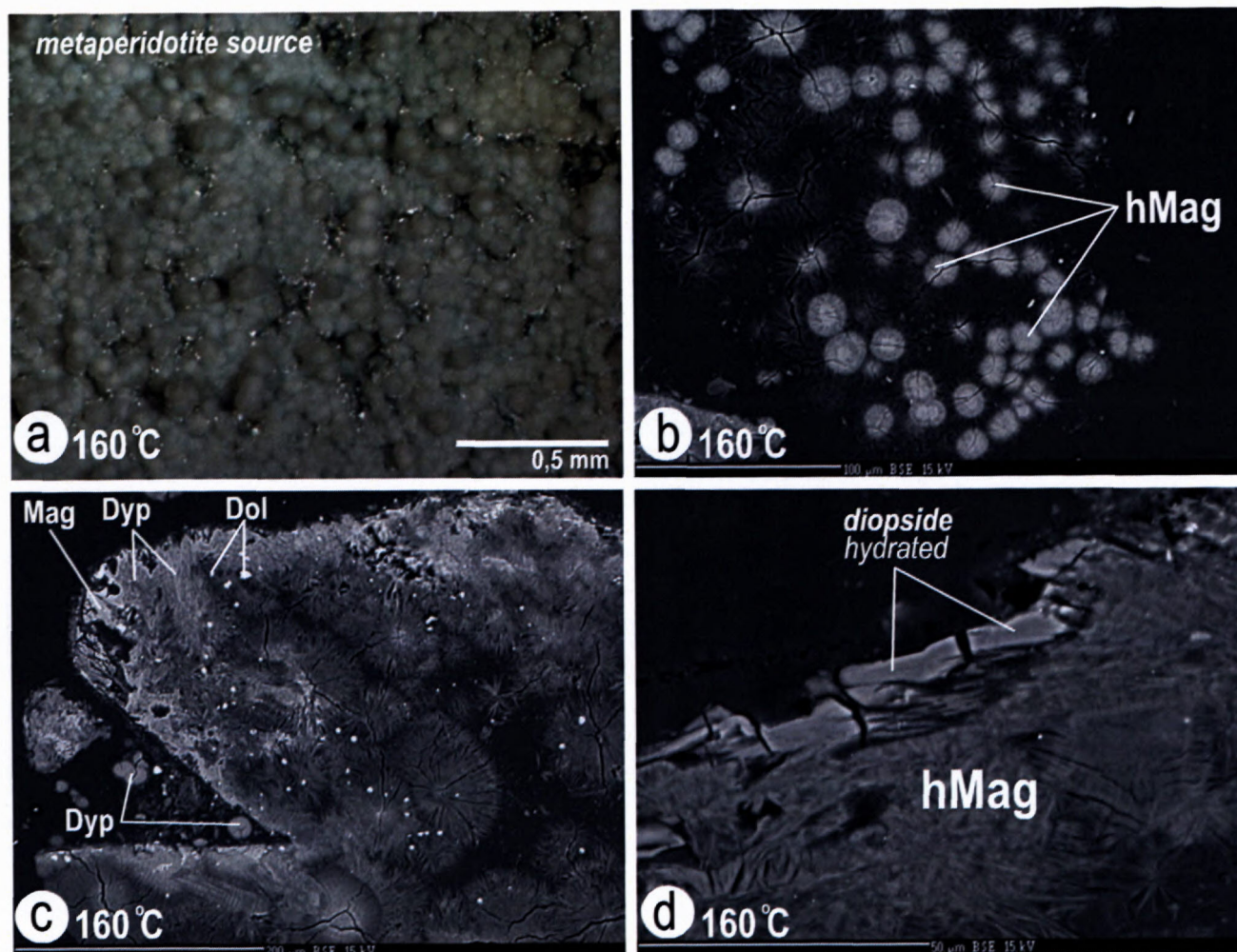


Fig. 5 Products of the artificial carbonatization were formed at temperature 160°C from the metaperidotite – serpentinite source. Sample HO – 2 a) hydromagnesite (hMag) in binocular loupe, b) hydromagnesite in back-scattered electron image, c) The relict of enstatite replaced by magnesite (Mag), dypingite (Dyp) and dolomite (Dol). Back-scattered electron image., d) relict of hydrated diopside replaced by hydromagnesite. Back-scattered electron image.

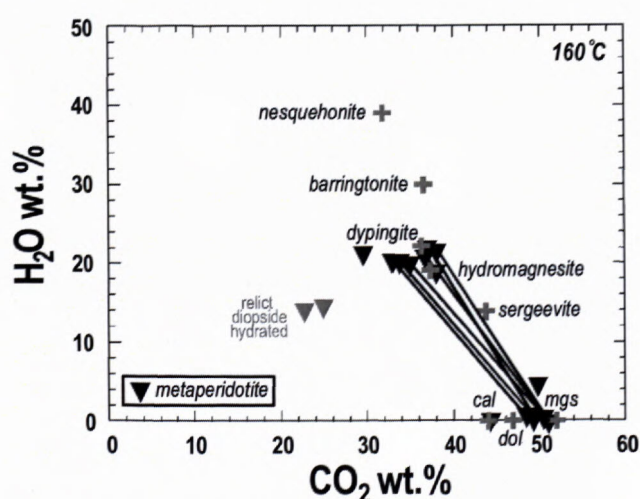


Fig. 6 Variation of H<sub>2</sub>O and CO<sub>2</sub> in coexisting dypindite, hydromagnesite, calcite, dolomite and magnesite. Sample HO-2. These minerals were formed during artificial carbonatization at temperature 160 °C from the metaperidotite source. Grey plus – contents of H<sub>2</sub>O and CO<sub>2</sub> in end member minerals: cal – calcite, dol – dolomite, mag – magnesite. Grey reverse triangle – content of H<sub>2</sub>O and CO<sub>2</sub> in hydrated relict of diopside.

### 5. Discussion

The reactions 6 - 9 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 CO<sub>2</sub> + H<sub>2</sub>O composition as well as according to new formed acid carbonates and carbonates. These reactions represent the artificial carbonation process, which can take place under various temperature conditions. A weight of carbon dioxide (kg) was calculated after the mass balance of these reactions. Consequently, it allows to asses the weight of CO<sub>2</sub> consumed in 1 m<sup>3</sup> of metaperidotite, metawehrlite or in metawebsterite during artificial carbonatization process. In the course of reaction 6 controlled by temperature 50°C is possible to consume 1 264 kg of CO<sub>2</sub> in 1 m<sup>3</sup> of metaperidotite, if the volume density of metaperidotite is 3.0 kg/m<sup>3</sup>. The capability of rock decreases to 1 083 kg of sequestered CO<sub>2</sub> in case of lower volume density 2.57 kg/m<sup>3</sup> that is the value typical for serpentinite.

In terms of reaction 7, when the temperature level is kept at the value 50°C, 1 m<sup>3</sup> of metawehrlite can elimi-



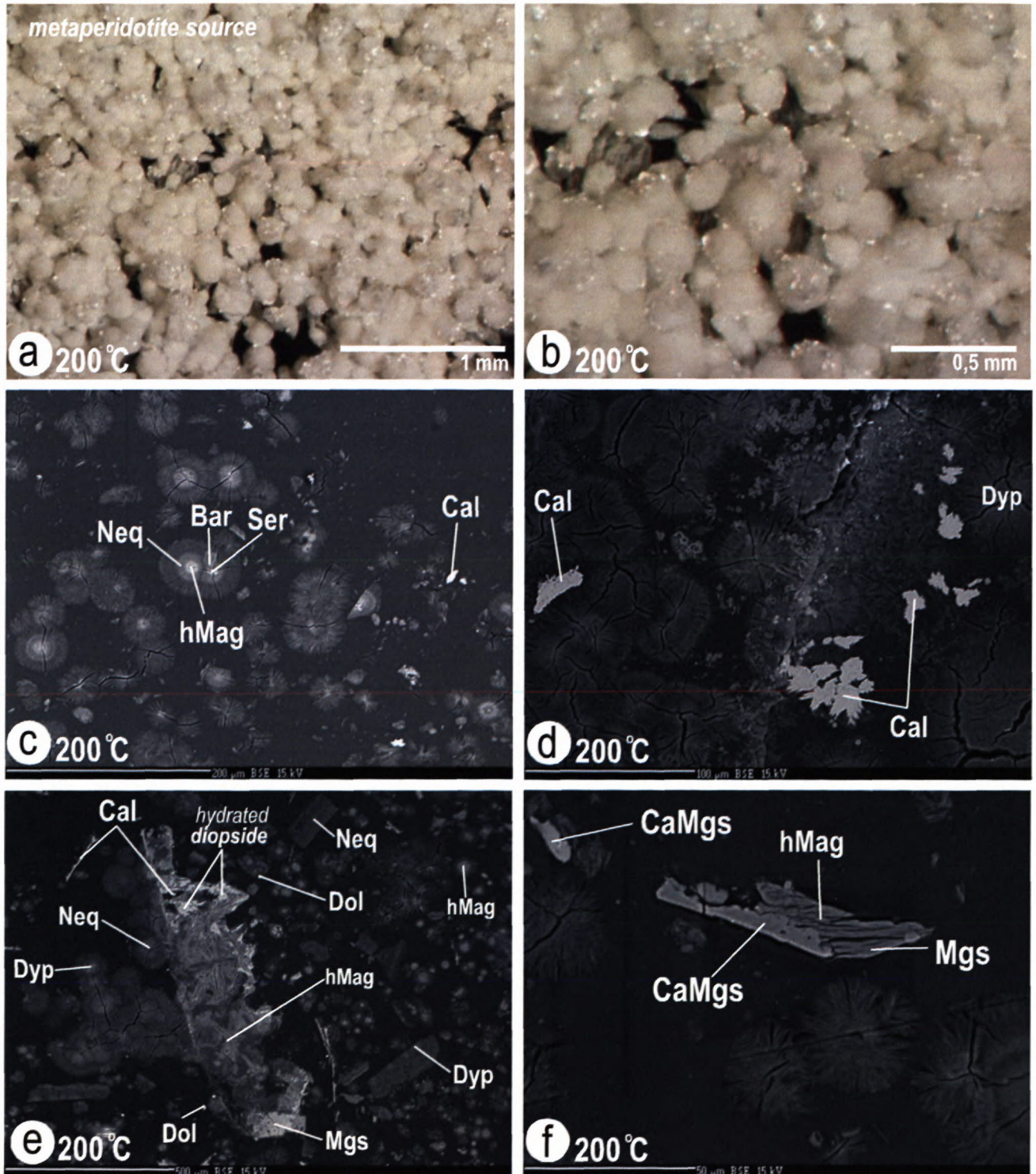


Fig. 7 Products of artificial carbonatization were formed at temperature 200 °C from the metaperidotite – serpentinite source. Sample HO-2., a) and b) spherical form of hydromagnesite (hMag), nesquehonite (Neq), barringtonite (Bar), sergeevite (Ser) and dypingite (Dyp) in binocular loupe, c) zonal grains of hydromagnesite (core), sergeevite (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 (Mag). Initial chrysotile (serpentine) was replaced by nesquehonite, hydromagnesite and dypingite. Back-scattered electron image., f) hydromagnesite, Ca magnesite (CaMag) and magnesite in back-scattered electron image.



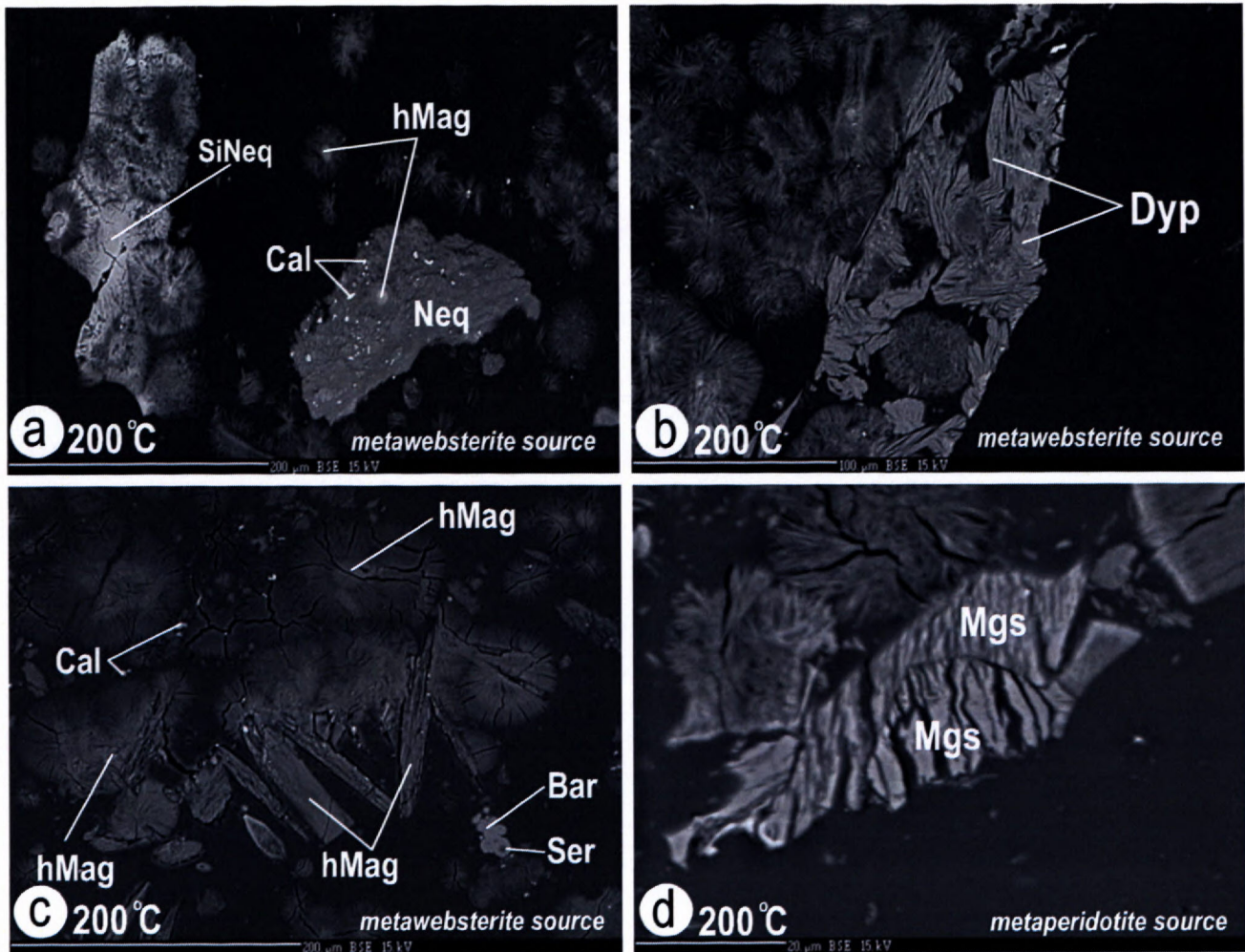


Fig. 8 Products of artificial carbonatization were formed at the temperature 200 °C from websterite source (a,b,c.) and from metaperidotite source (d). Samples RU-1, RU-2 and HO-3., a) hydromagnesite (hMag) nesquehonite (Neq), Si nesquehonite (Si Neq) and calcite (Cal) in back-scattered electron image., b) enstatite grain replaced by dypingite (Dyp). Back-scattered electron image., c) calcite, idiomorphic and zonal grain of hydromagnesite, spherical form of barringtonite (Bar) and sergeevite (Ser) in back-scattered electron image., d) magnesite (Mgs) in back-scattered electron image.

nate 902 kg of CO<sub>2</sub> if the volume density of metawehrlite is 2.57 kg/m<sup>3</sup>, or 1 053 kg when its volume density reaches 3.0 kg/m<sup>3</sup>. Completely serpentinised wehrlite exhibits the same volume density as the serpentinised peridotite ( $\rho = 2.57 \text{ kg/m}^3$ ).

The peridotite carbonatization process in conformity with reaction 8 at temperature 160 °C as well as 200 °C consumes 1 174 kg of CO<sub>2</sub>, alternatively, 1 006 kg of CO<sub>2</sub> in 1 m<sup>3</sup> of rock in dependence on minimum, or maximum substance of serpentine group in peridotite. According to the same dependence balanced in reaction 9, the 1 m<sup>3</sup> of metawebsterite eliminates 1 078 kg of CO<sub>2</sub> or 924 kg of CO<sub>2</sub> similar to the metaperidotite ability at the same temperature 200 °C. 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 CO<sub>2</sub> eliminated in 1 m<sup>3</sup> of metaperidotite, metawehrlite and metawebsterite the consumed weight of carbon dioxide ranges from 902 kg to 1 264 kg and does not depend neither 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 to 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.

## 6. Conclusion

The capability of metaperidotite (locality Komárovce – Hodkovce), metawehrlite (locality Jasov) and metawebsterite (locality Rudník) to eliminate an industrial CO<sub>2</sub> emissions have been verified by the experimental study of artificial carbonatization. Laboratory tests have been carried out at prepared samples of ultramafic rocks from above mentioned localities. Serpentinite was mixed with water by temperature 22 °C, when was changed the pressure of carbon dioxide from 0.1 to 0.3 MPa and the time from 5 to 20 hours during reactions. The acid carbonates (nesquehonite, barringtonite, dypingite, hydro-



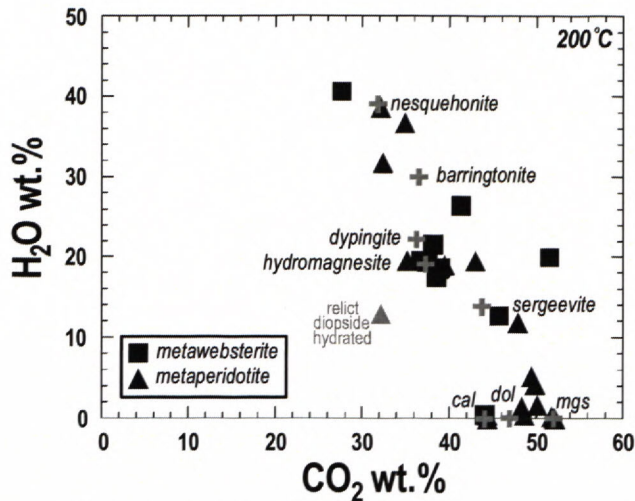


Fig. 9 Variation of  $H_2O$  and  $CO_2$  in coexisting acid carbonates: nesquehonite, barringtonite, dypingite, hydromagnesite, sergeevite and carbonates: calcite, dolomite and magnesite. These minerals were formed during artificial carbonatization at temperature  $200\text{ }^\circ\text{C}$  from the metaperidotite source (sample HO-2) and from metawebsterite source (sample RU-1 and RU-2). Grey plus –  $H_2O$  and  $CO_2$  contents in end member minerals: cal – calcite, dol – dolomite, mag – magnesite. Grey triangle –  $H_2O$  and  $CO_2$  content in hydrated diopside.

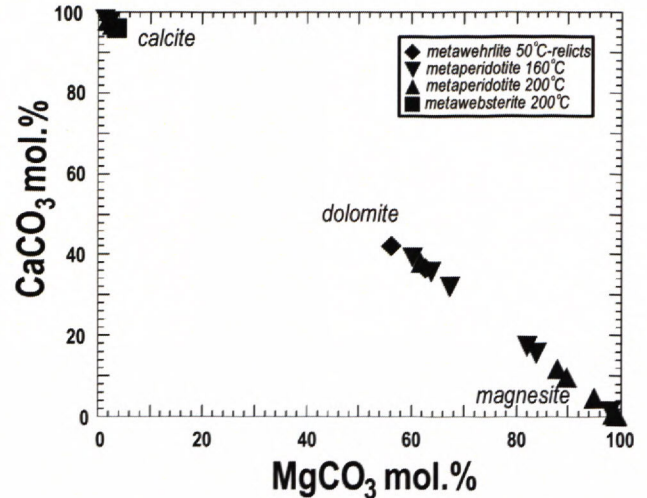


Fig. 10 Variation of  $CaCO_3$  and  $MgCO_3$  in carbonates. These minerals crystallized at the expenses silicates in various mantle rocks. Dolomite and calcite are relicts of the source metawehrlite, stable at  $50\text{ }^\circ\text{C}$ .

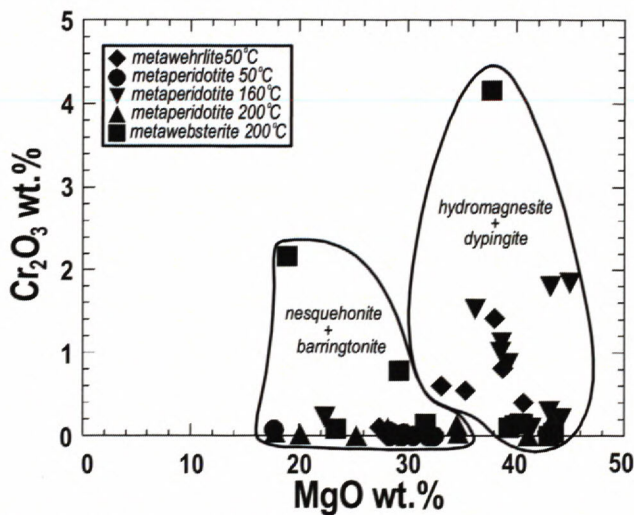
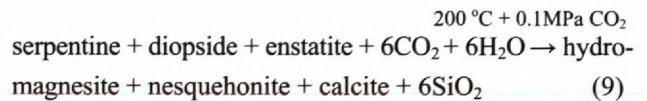
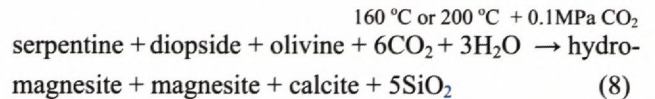
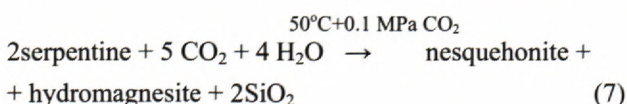
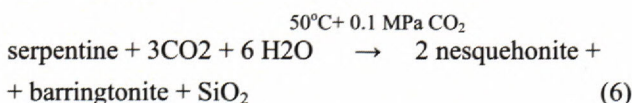


Fig. 11 Variation of  $Cr_2O_3$  and  $MgO$  in nesquehonite, barringtonite, dypingite and hydromagnesite.  $Cr_2O_3$  indicates molecule stichtite presence  $Mg_6Cr_2(OH)_{16}(CO_3)_4(H_2O)$  in these minerals.

magnesite), as well as carbonates (calcite, dolomite, and magnesite) crystallized from filtrate with pH value about of 8, during 4 – 24 hours (the dependency on the various temperatures).

This group of new minerals crystallized according to following reactions:



The reactions 6, 7, 8 and 9 served as the base for  $CO_2$  weight calculation that resulted to the final conclusion - how many kg of carbon dioxide is capable  $1\text{ m}^3$  of serpentinite to bond in its volume, during different temperature regimes. In comparison of ideal weight of  $CO_2$  liquidated in  $1\text{ m}^3$  of metaperidotite, metawehrlite and metawebsterite the sequestered weight of carbon dioxide from 902 kg to 1 264 kg does not depend neither the temperature condition of artificial carbonatization nor the type of the source rock. The gradual temperature increases from  $50\text{ }^\circ\text{C}$  through  $160\text{ }^\circ\text{C}$  to  $200\text{ }^\circ\text{C}$  has influence to higher share carbonates formation (calcite, dolomite, and magnesite) at the expense of acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite). Acid carbonates are dominating by temperature  $50\text{ }^\circ\text{C}$  while higher temperatures serve as a suitable environment for carbonates formation.

Results of experimental study show that serpentinite rocks are a suitable eliminator of  $CO_2$  especially in the Eastern part of Slovakia. Achieved results represent a solid base for better understanding the artificial carbonatization.

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