

**Permanent disposal of CO₂ industrial emission
via artificial carbonatization of metaperidotite,
metawehrlite and metawebsterite:
an experimental study**

by

**Martin Radvanec, Ľubomír Tuček, Katarína Čechovská,
Ján Derco & Ľudovít Kucharič**

Dionýz Štúr State Institute of Geology, Bratislava, Slovakia

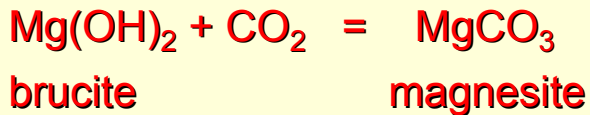
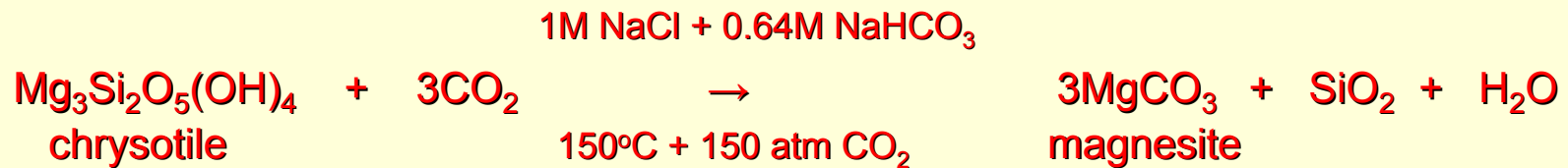
*For more and detail information see pages 53 - 65
in Slovak Geological Magazine, 2008*

Goals

- The presentation extends an experimental base of 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 (metalherzolite), metawehrlite and metawebsterite were subjected to reaction with water and CO₂ and therefore 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 of CO₂ can be sequestered in 1 m³ of the source metaperidotite, metawehrlite and metawebsterite.

Carbonatization

The serpentine group (chrysotile) reacts with CO₂ to produce magnesite during its carbonatization in atmosphere conditions (Herzog, 2002, Drobek et al., 2008). However, a process of artificial carbonatization uses NaCl and NaHCO₃ to produce intermediate product of MgCl₂ + Mg(OH)₂ and consequently, the final carbonatization reactions are following :



- Therefore Serpentinite bodies are efficient in CO₂ storage.
- Those bodies which were not influenced by natural CO₂ 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.

Mineral composition of source mantle rocks (serpentinite) used for artificial carbonatization

Metaperidotite bodies located in the East Slovakia

- **Metawebsterite** is formed by antigorite + chrysotile (75 %), Al-enstatite + Al-dioside ± fayalite (15 %), magnetite prevails over oxide mineral association: pyrophanite + Mn-rutile + Cr-magnetite (together 5 %); calcite (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 (?) + andratite + 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 + andratite + ernienickelite + Cr-chlorite.
- **Metaperidotite** is formed by chrysotile (80 vol. %), olivine + enstatite + diopside (10 %), calcite and dolomite (1.3 %), magnetite and hematite (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.

Sample preparation, analytical methods and experimental conditions

- Serpentinite was mixed with water and carbon dioxide according to the procedure used by Tuček et al., (2009).
- Stable temperature, 22 °C and CO₂ 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 were formed at temperatures 50 °C, 160 °C and 200 °C.
- The crystallization time was from 4 to 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), by 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.

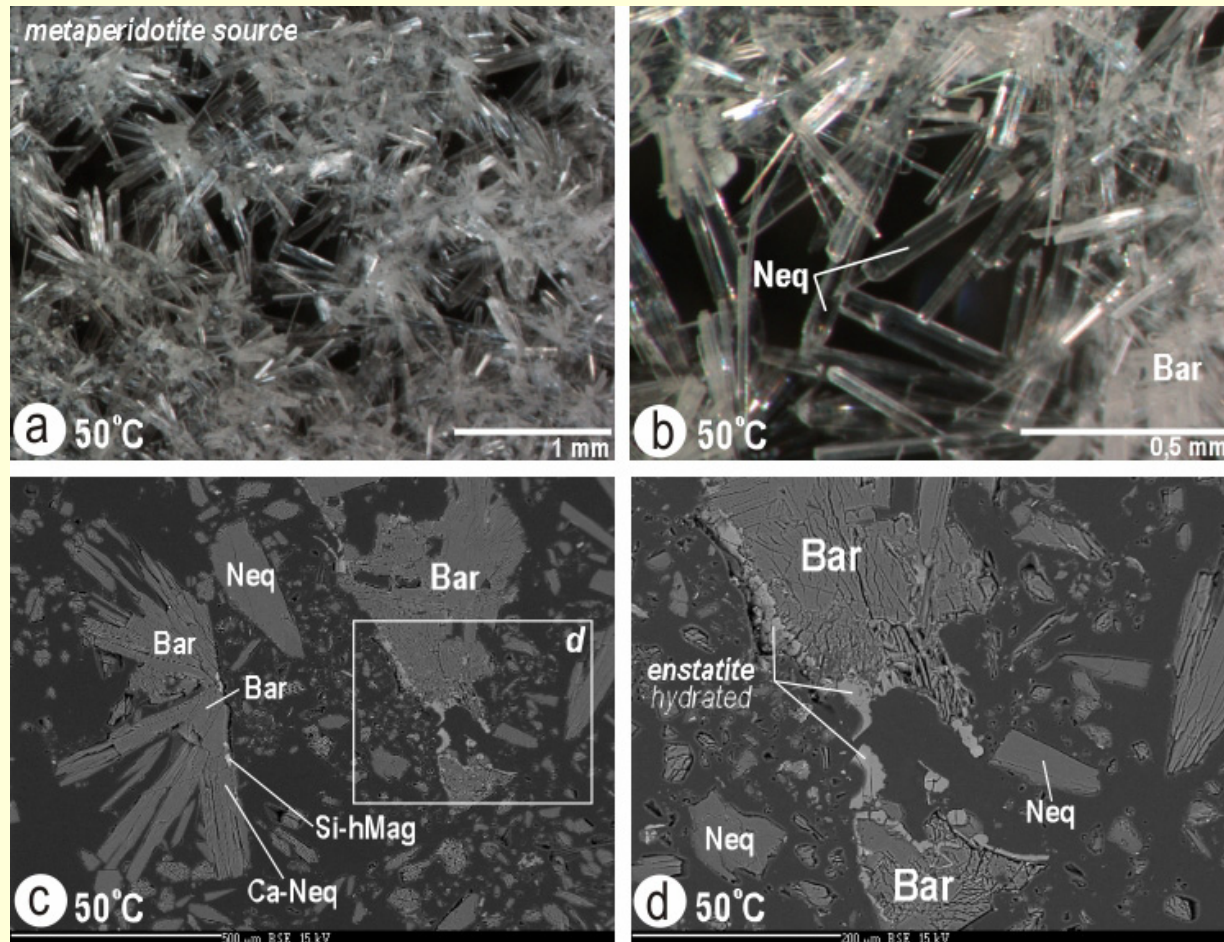
Minerals of artificial carbonatization formed at temperature 50 °C

a) nesquehonite (Neq) in binocular loupe

b) nesquehonite and barringtonite (Bar) in binocular loupe

c) 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



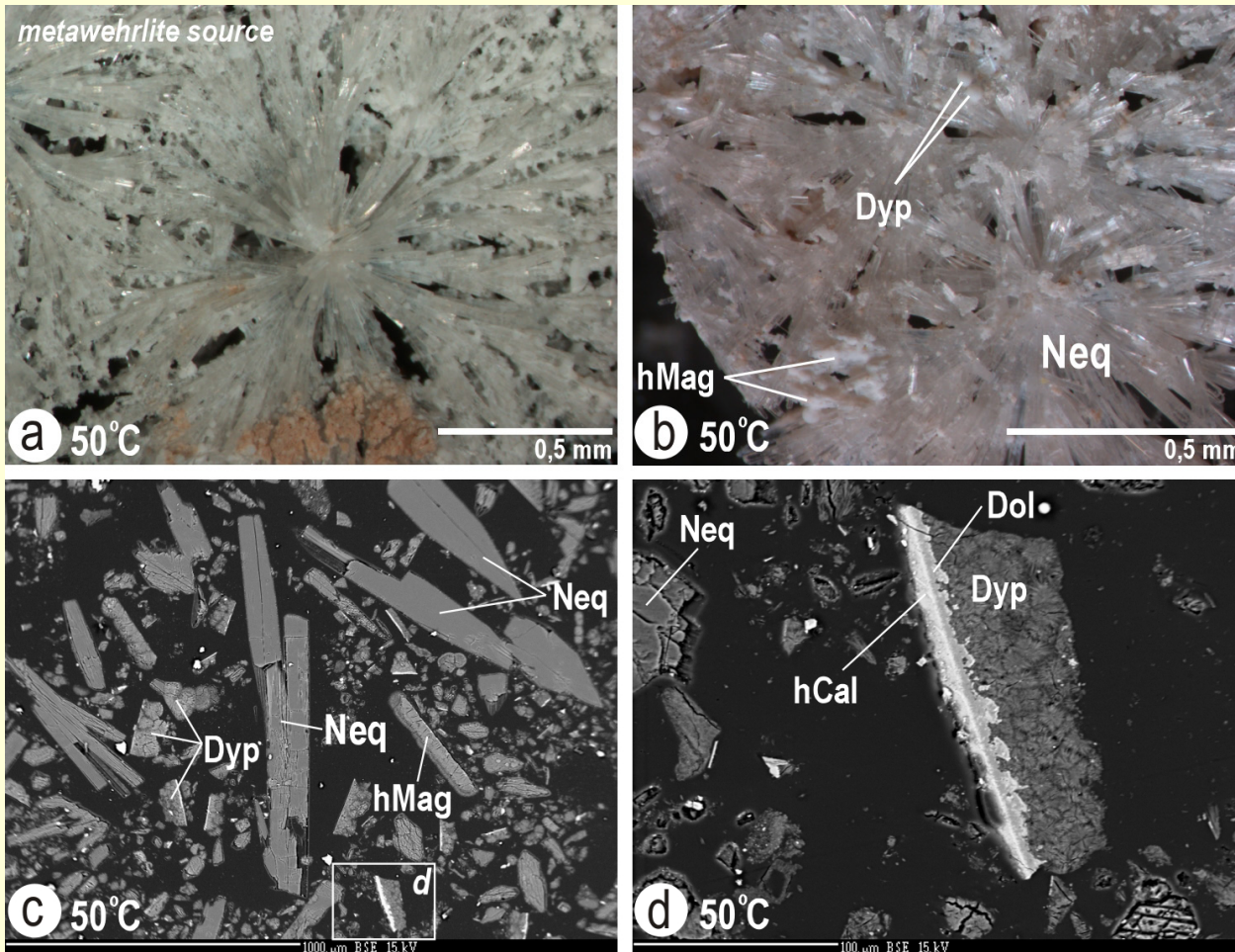
Minerals of artificial carbonatization formed at temperature 50 °C

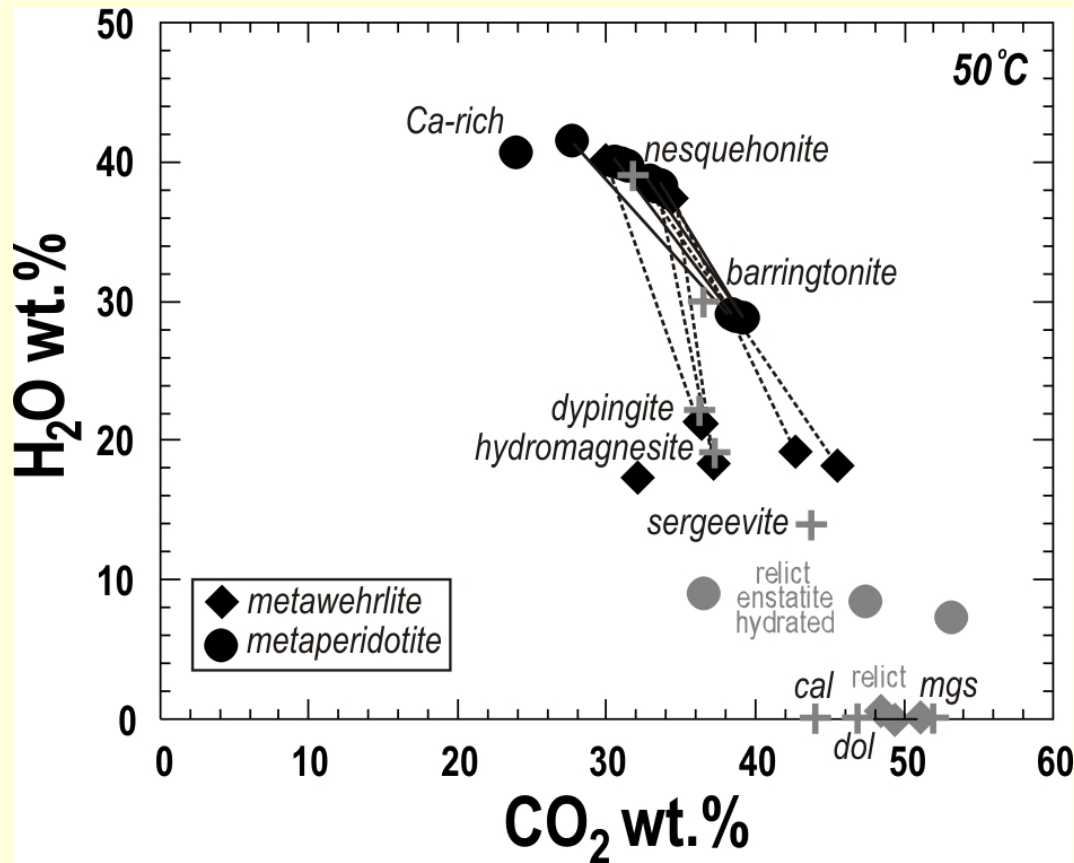
a) nesquehonite (Neq) and dypingite (Dyp) in binocular loupe

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, Back-scattered electron image





Variation of H₂O and CO₂ in coexisting pair of nesquehonite – barringtonite (metaperidotite source) and in coexisting pair nesquehonite – dypingite/hydromagnesite (metawehrlite source).

Grey plus – contents of H₂O and CO₂ in end member minerals: cal – calcite, dol – dolomite, mgs – magnesite.

Grey circles - contents of H₂O and CO₂ in hydrated relict of enstatite.

Grey rhomb – carbonate relics from original metawehrlite.

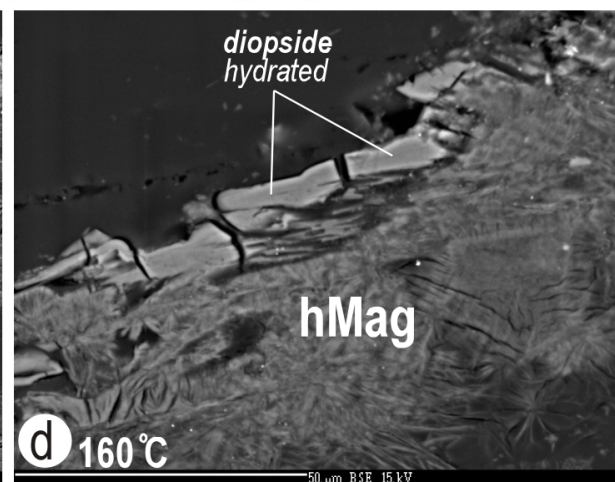
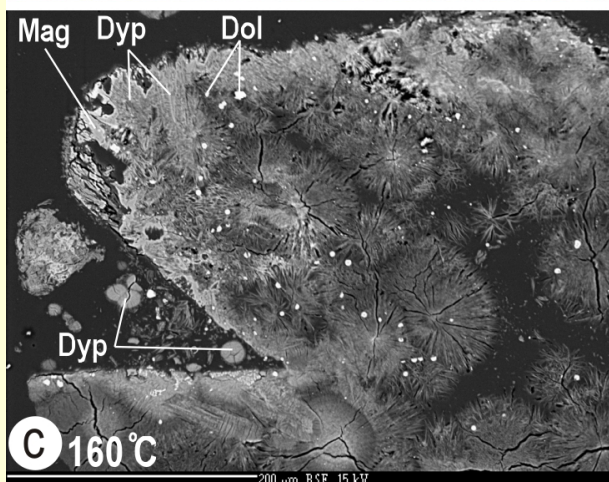
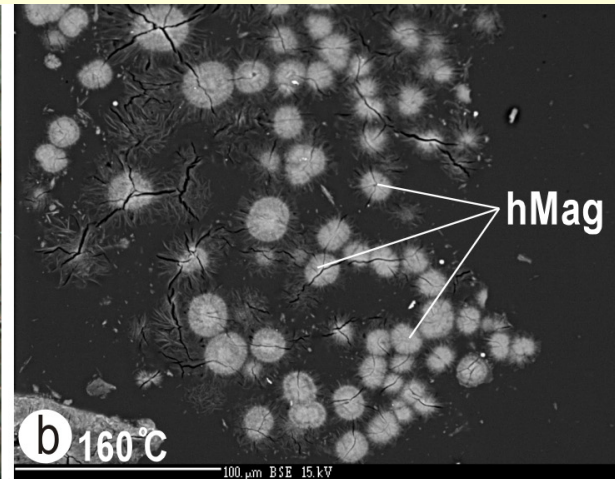
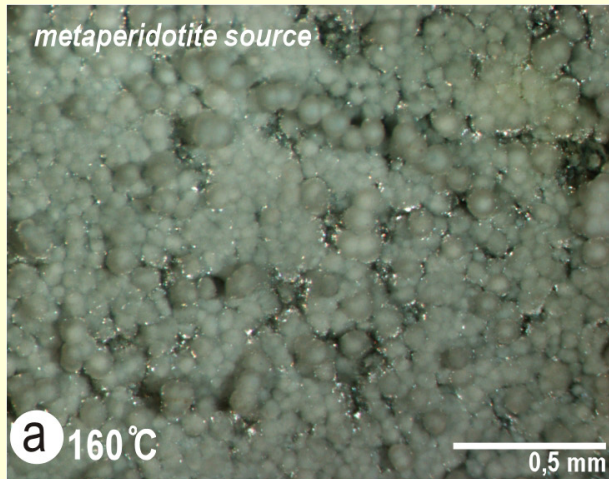
Minerals of artificial carbonatization formed at temperature 160 °C

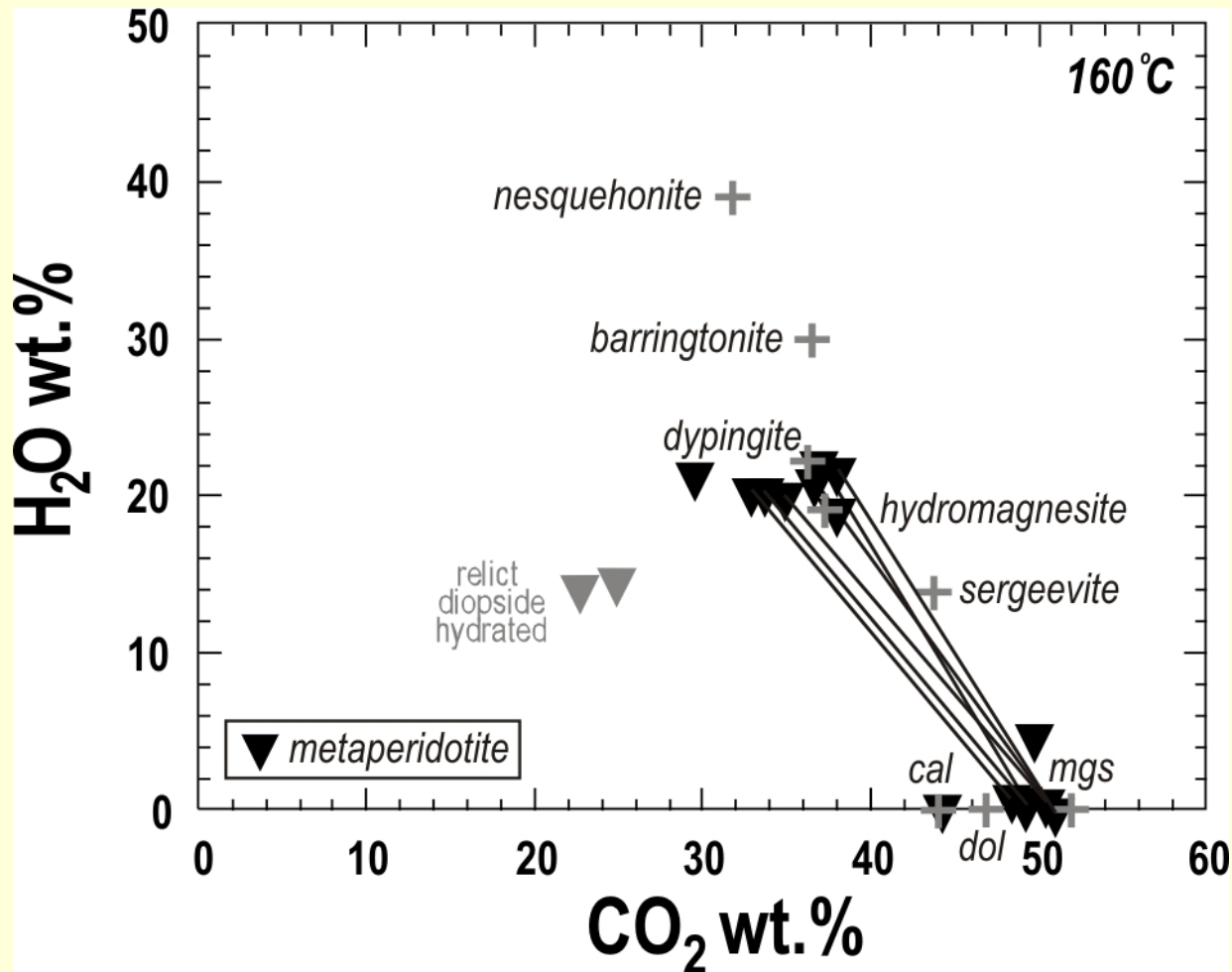
a) hydromagnesite (hMag) in binocular loupe

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) relic of hydrated diopside replaced by hydromagnesite. Back-scattered electron image.





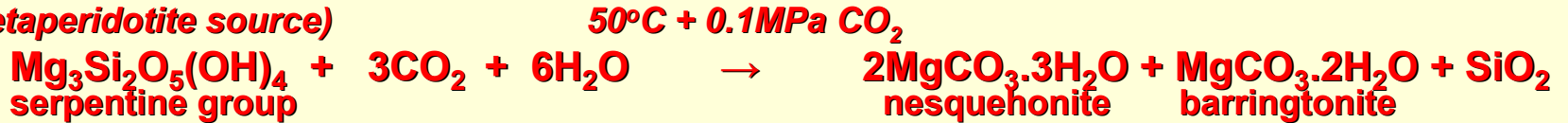
Variation of H₂O and CO₂ in coexisting dypindite, hydromagnesite, calcite, dolomite and magnesite..

Grey plus – contents of H₂O and CO₂ in end member minerals: cal – calcite, dol - dolomite, mgs – magnesite

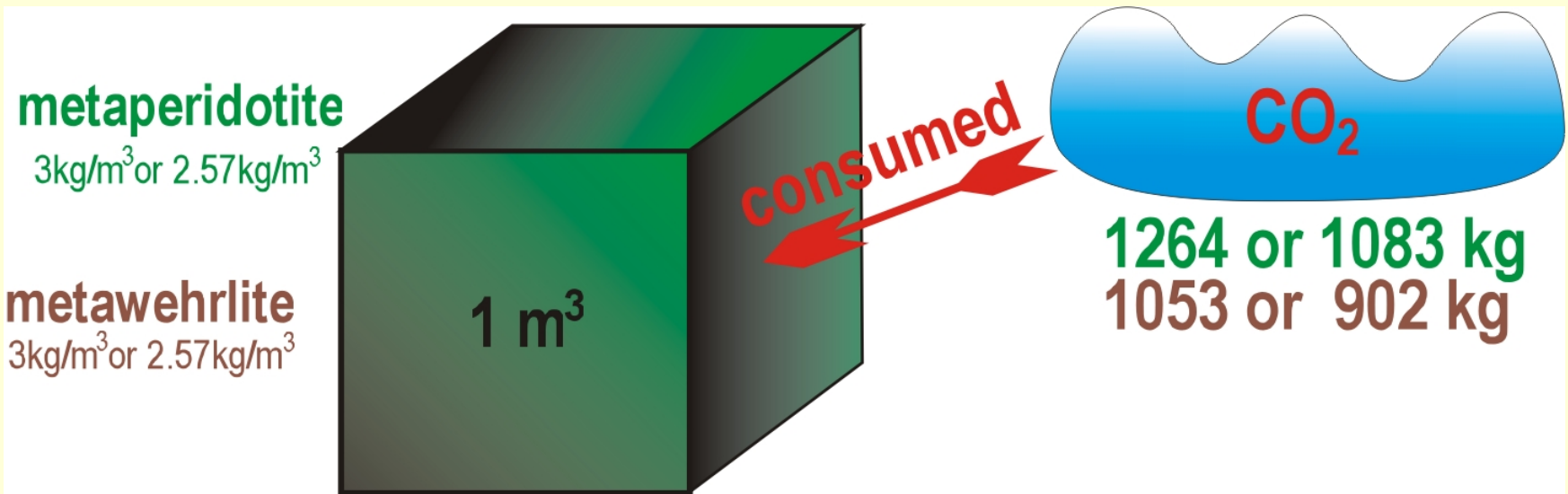
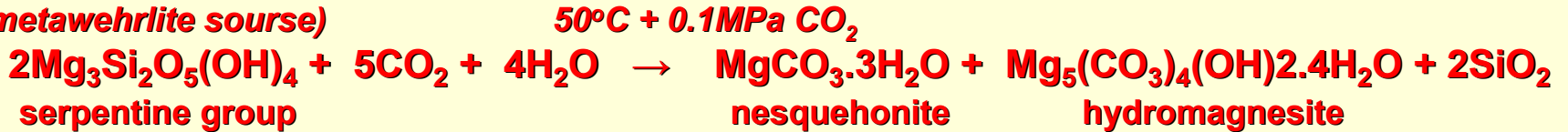
Grey reverse triangle – content of H₂O and CO₂ in hydrated relict of diopside.

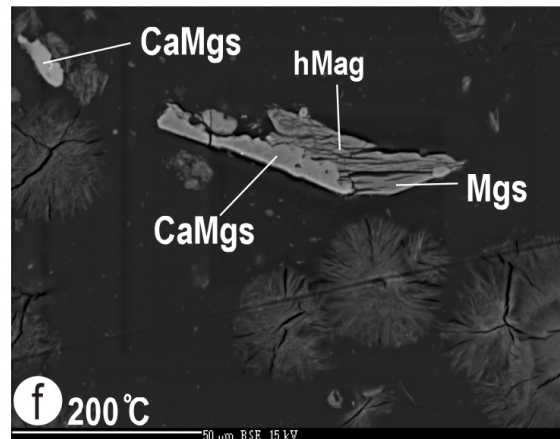
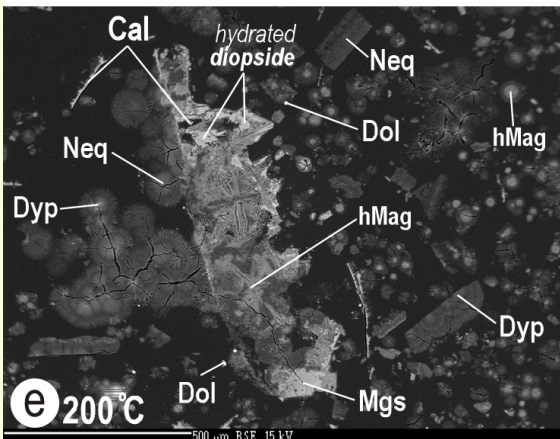
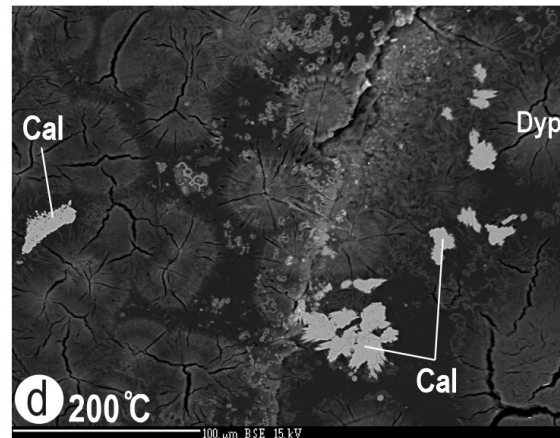
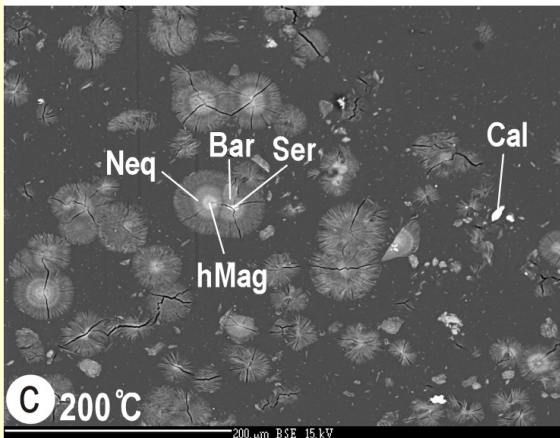
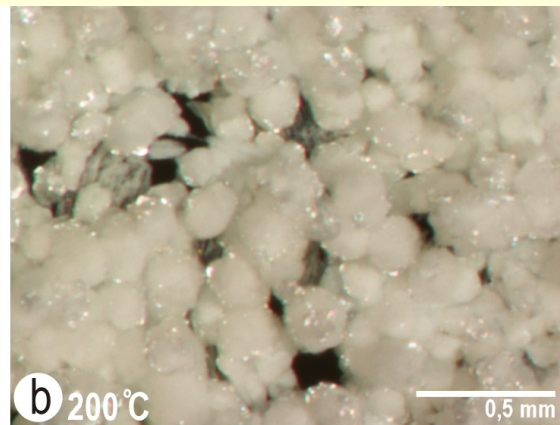
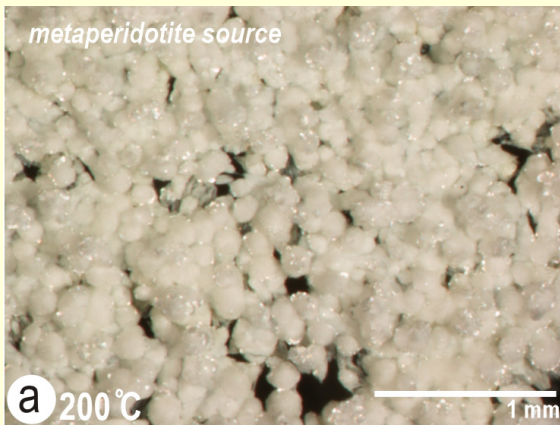
Results in reactions at 50 °C

(metaperidotite source)



(metawehrlite source)



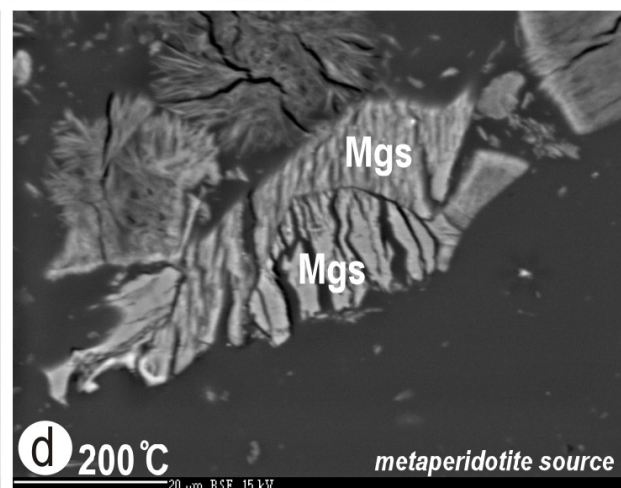
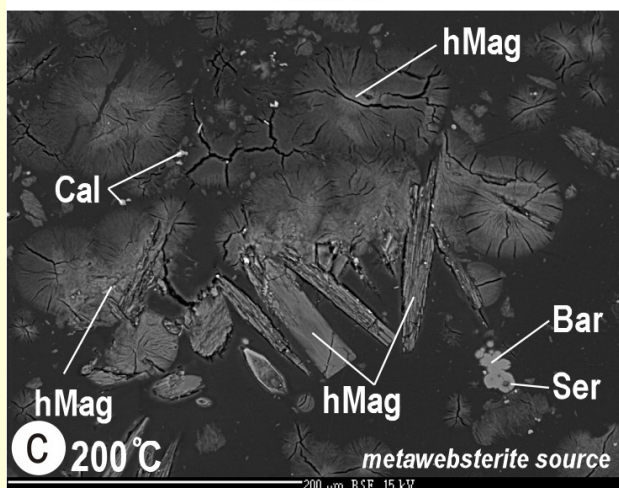
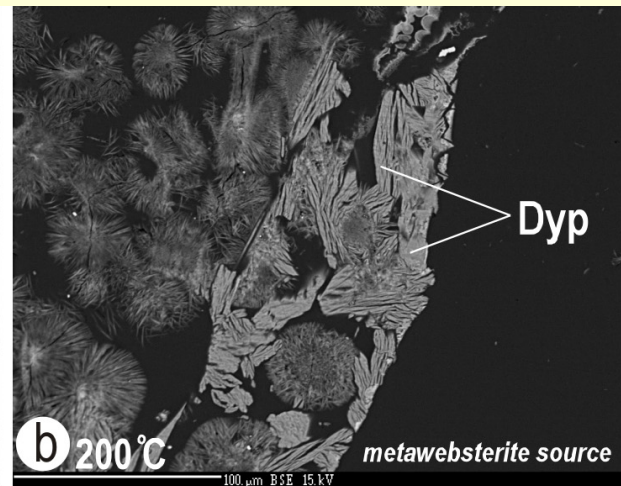
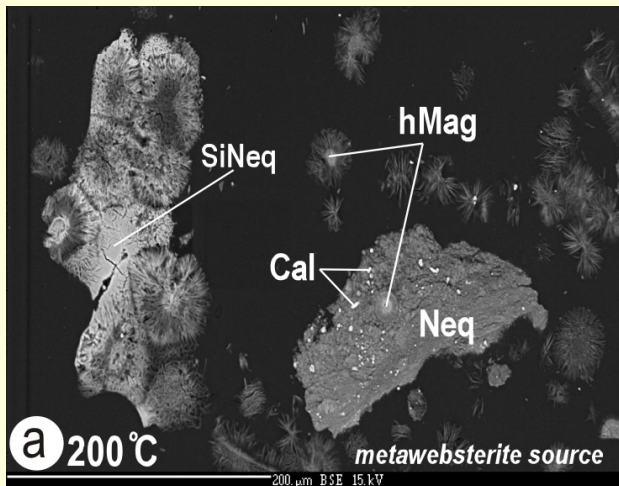


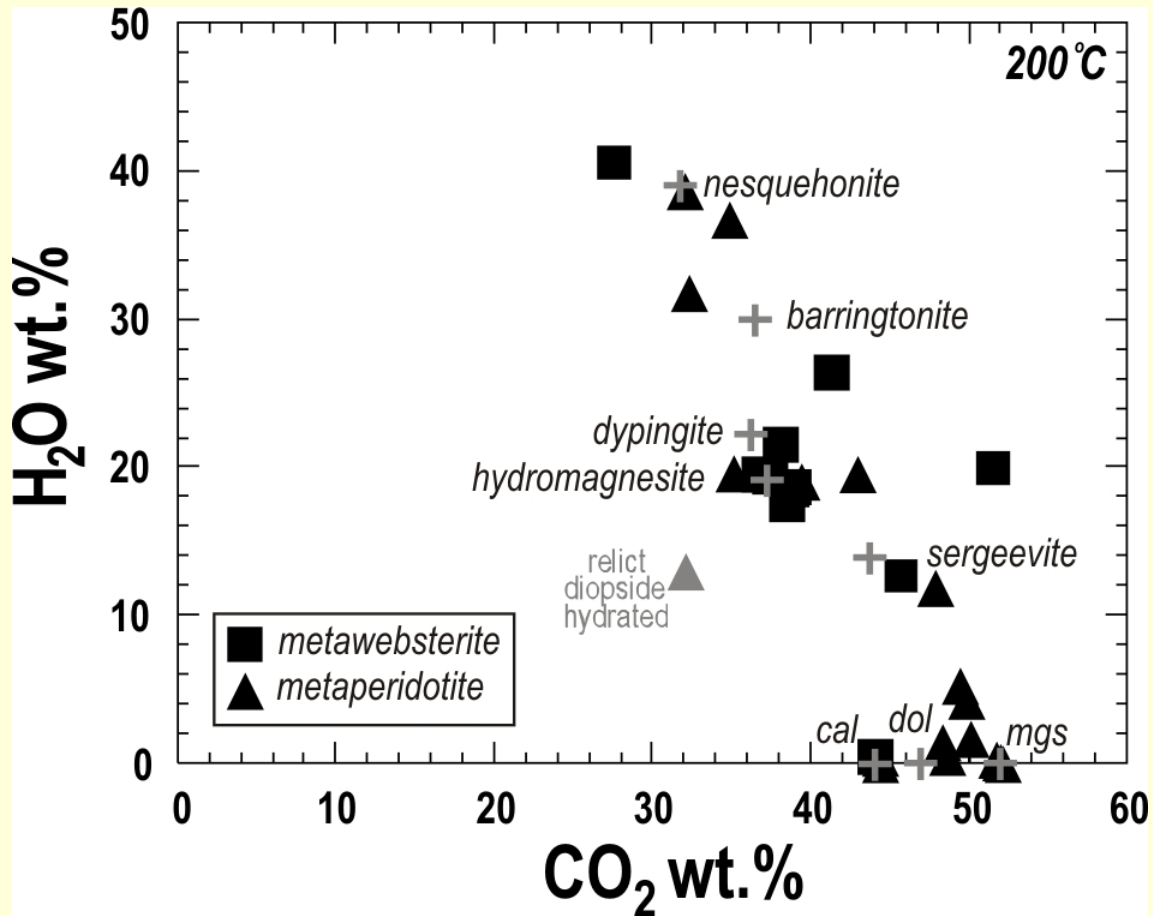
Minerals of artificial carbonatization formed at temperature 200 °C

- a) and b) 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.

Minerals of artificial carbonatization formed at temperature 200 °C from websterite source (a,b,c,) and from metaperidotite source (d).

- 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, hydromagnesite, barringtonite (Bar) and sergeevite (Ser) in back-scattered electron image.
- d) magnesite (Mgs) in back-scattered electron image.

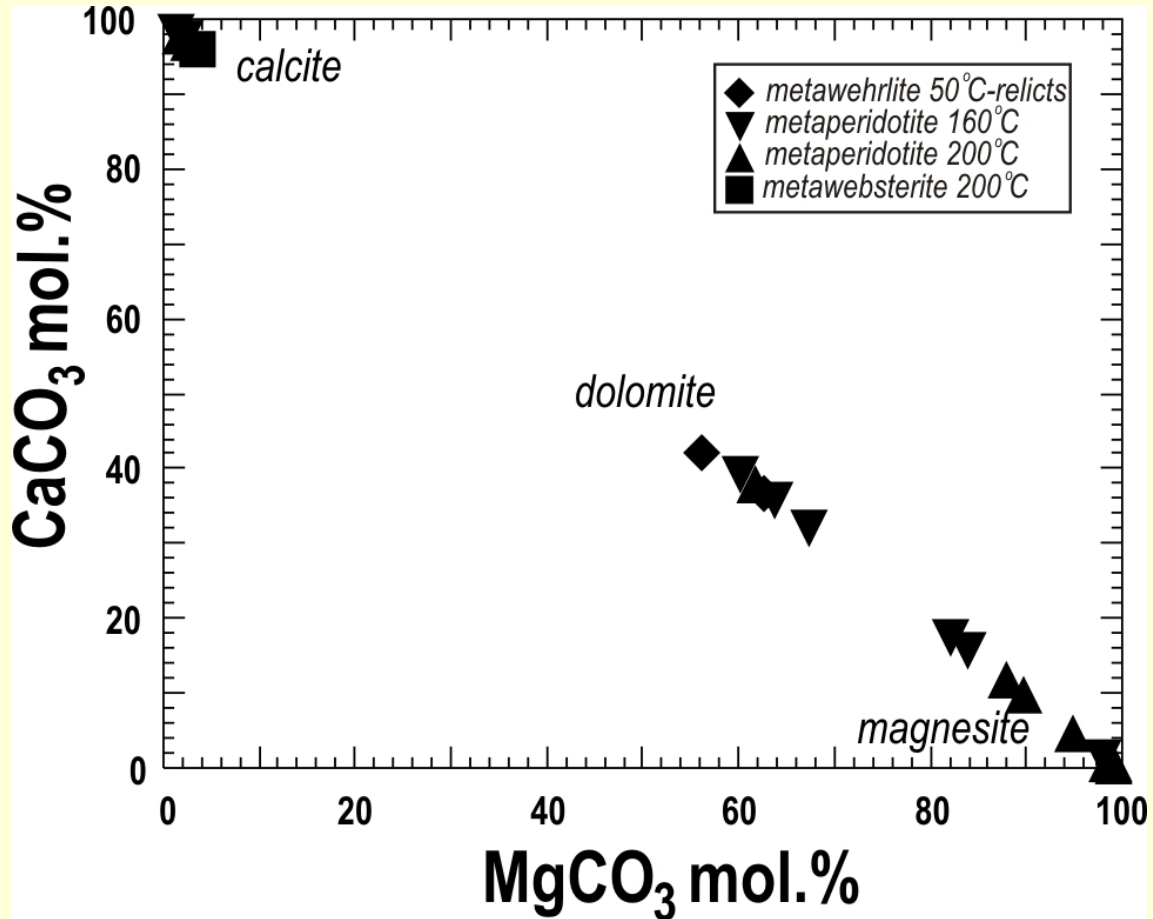




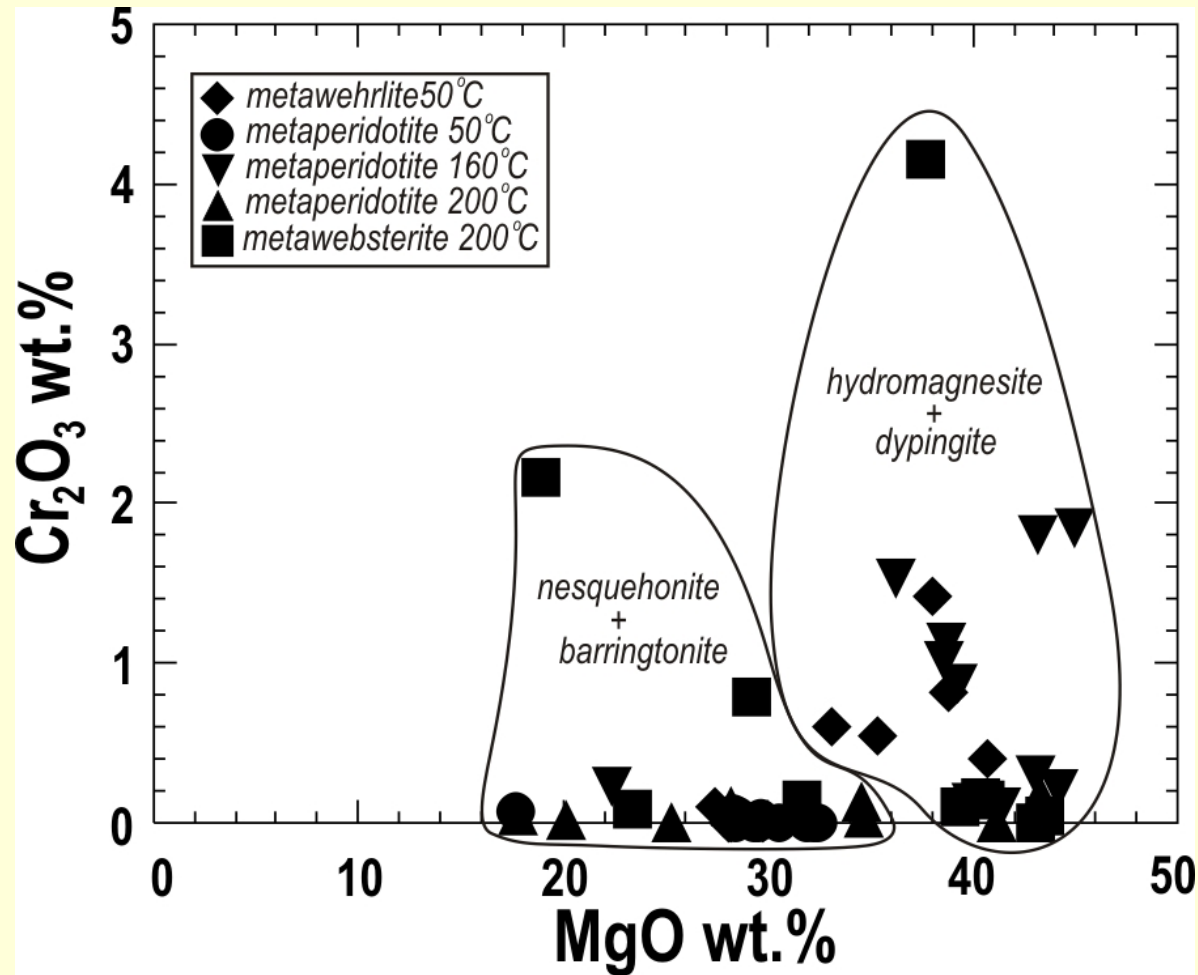
Variation of H₂O and CO₂ in coexisting acid carbonates: nesquehonite, barringtonite, dypingite, hydromagnesite, sergeevite and carbonates: calcite, dolomite and magnesite.

Grey plus - H₂O and CO₂ contents in end member minerals: cal – calcite, dol – dolomite, mgs – magnesite.

Grey triangle - H₂O and CO₂ content in hydrated diopside.



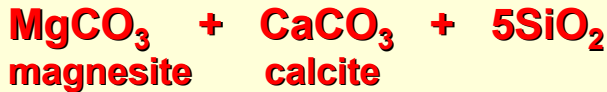
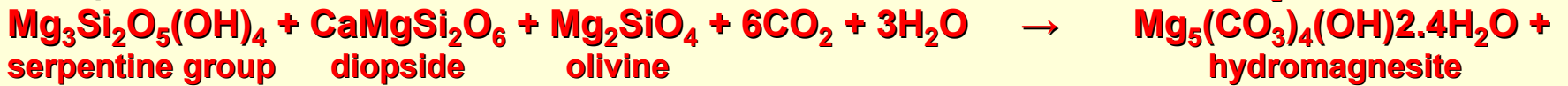
Variation of CaCO₃ and MgCO₃ in carbonates. These minerals crystallized at the expenses silicates in various mantle rocks. Dolomite and calcite are relicts of the source metawehrlite, stable at 50 °C.



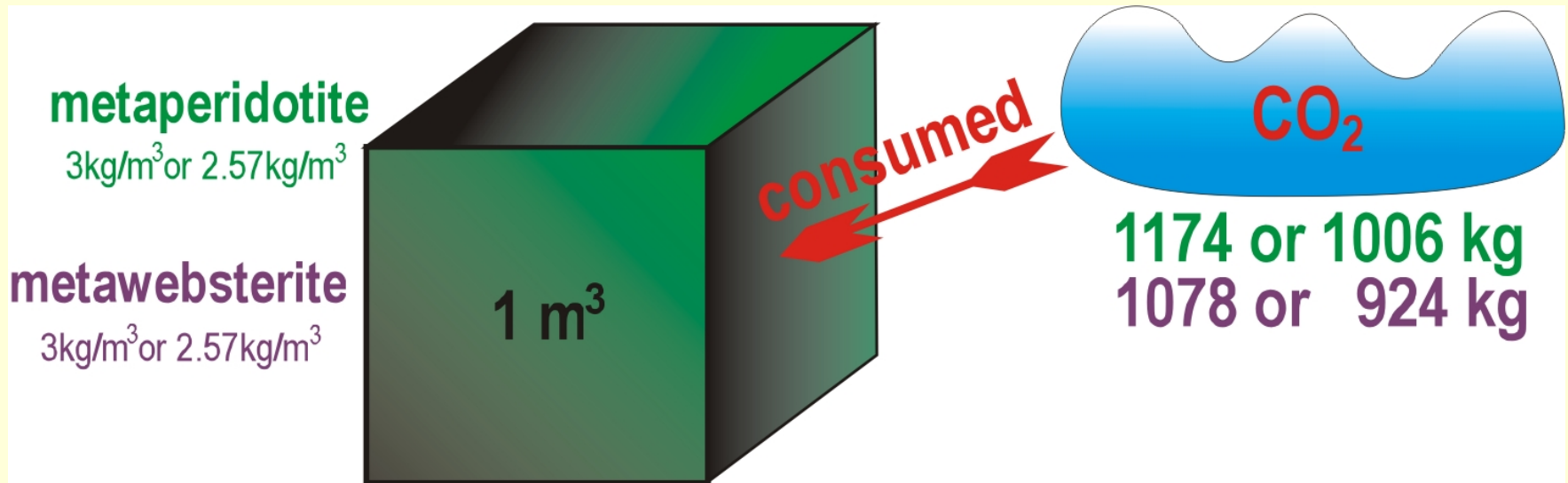
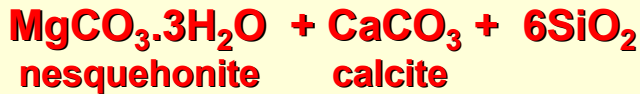
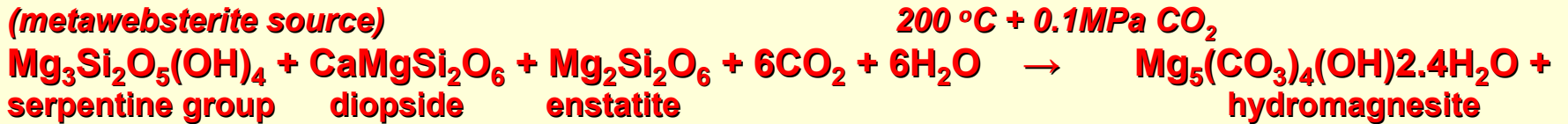
Variation of Cr₂O₃ and MgO in nesquehonite, barringtonite, dypingite and hydromagnesite. Cr₂O₃ indicates molecule stichtite presence Mg₆Cr₂(OH)₁₆(CO₃)₄·4(H₂O) in these minerals.

Results in reactions at 160 °C and 200 °C

(metaperidotite source)



(metawebsterite source)



Conclusions

- 1 m³ of metaperidotite, metawehrlite and metawebsterite consumed the weight of carbon dioxide from 902 kg to 1 264 kg.
- The consumed weight does not depend neither on the temperature condition of artificial carbonatization nor on the type of the source rock.
- The gradual temperature increases from 50 °C through 160 °C to 200 °C and it has influence to higher share of carbonates formation (calcite, dolomite, and magnesite) than acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite) formed at lower temperature.
- Acid carbonates are dominating by temperature 50 °C while higher temperatures serve as a suitable environment for carbonates formation.
- Results of experimental study show that serpentinite rocks are a appropriate eliminator of CO₂ especially in the Eastern part of Slovakia.
- Achieved results represent a solid base for better understanding the process of artificial carbonatization.