



CO₂ sequestration by carbonatization:

Origin of new stable
products using
serpentinite

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Mineral sequestration

1. Theory





QUALITY of ATMOSPHERE – GRADUAL DETERIORATION by extensive release of CO₂ into atmosphere

Main producers of CO₂ in Slovakia (183 producers;
limits for 2008 41.261 mil. t.):



1. **Electrical and heating industries**

(e.g. electrical plant in Eastern Slovakia 5.36 mil. t. in 2008)

2. **Metallurgical industry and steelworks**

(11.4 mil. t. in 2008)

3. **Industry where the carbonate-bearing raw material is decomposed by heat**

(limekilns, magnesite dressing plants, cement factories)

4. **Traffic (mainly automobile transport)**

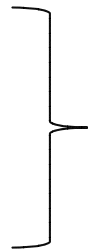
(2.45 mil. t. in 2008 - production of petrol)

5. **Combustion of waste**



Definition of CO₂ sequestration :

1. catching
2. deposition
3. storing



CARBON DIOXIDE



CO₂ sequestration:

- physical method (e.g. geological storing)
- biological method (e.g. reforestation)
- chemical method (e.g. mineral sequestration)



Catching of CO₂ = its removal

- from combustion gas
- from technological gas or atmosphere

Obtaining of high purity CO₂ (above 98 %),
which can be:

- used
- converted
- stored





Separation of CO₂ from:

- nitrogen oxides (NO_x)
- sulphur oxides (SO_x)
- carbon oxide (CO)
- oxygen (O₂)
- water vapour (H₂O)
- other gass compounds (methane, hydrosulphide)
- solid particles



can be done by numerous methods and ways



CO₂ sequestration by carbonatization - safe method of liquidation of industrial CO₂

**Simplified principle of carbonatization -
exothermic reaction:**



**Final result of reactions →
solid and stable products - carbonates**



Mineral carbonatization:

- direct method (single-phase method)
- indirect method (two-phase method)

Direct method:

Reacting mineral components directly enter into the reaction with CO_2

Indirect method:

mineral (reacting) components are extracted from mineral matrix and consequently react with CO_2





Natural conditions –

mineral carbonatization (especially direct) represents
very slow process

To **accelerate reactions:**

- inevitable technological **optimization of all factors**, influencing the reaction kinetics

Modification of entering mineral compounds –

- grain-size,
- thermic,
- chemical,
- physical–mechanical or their combination.



General factors, influencing to reaction rate and forming of final products:

- mineral and chemical composition of entering rocks (activity of their components, purity of gass regarding CO₂)
- state of entering components, their mutual ratio
- **temperature (T)**
- **pressure (p) CO₂**
- **reaction time** – time of mutual activity of phases with CO₂
- grain-size, porosity and activity of specific surface of material
- modification of entering components (chemical, thermic, ...)
- reaction conditions – static or dynamic
- pH of reaction environment
- type of additives, reagents,...
- density, resp. viscosity of reacting suspension



Advantages of mineral sequestration of CO₂:

- CO₂ is firmly tied on qualitatively new and stable products
- **Prepared products - carbonates are safe for environment**
- Reactions with CO₂ resulting in carbonate origin are exothermic
- Liquidation (change) on final products occurs in relatively short time
(1 hour till 2 days)
- Carbonates can be deposited and stored unlimitedly long time
- Finances for expensive monitoring are saved
- Waste (CO₂) reacts with other (harmful) waste (e.g. serpentinite) and useful matter originates (protection of environment)
- New mineral compounds can be used in various industrial branches (anorganic filling agents – plastics, colours, ...)



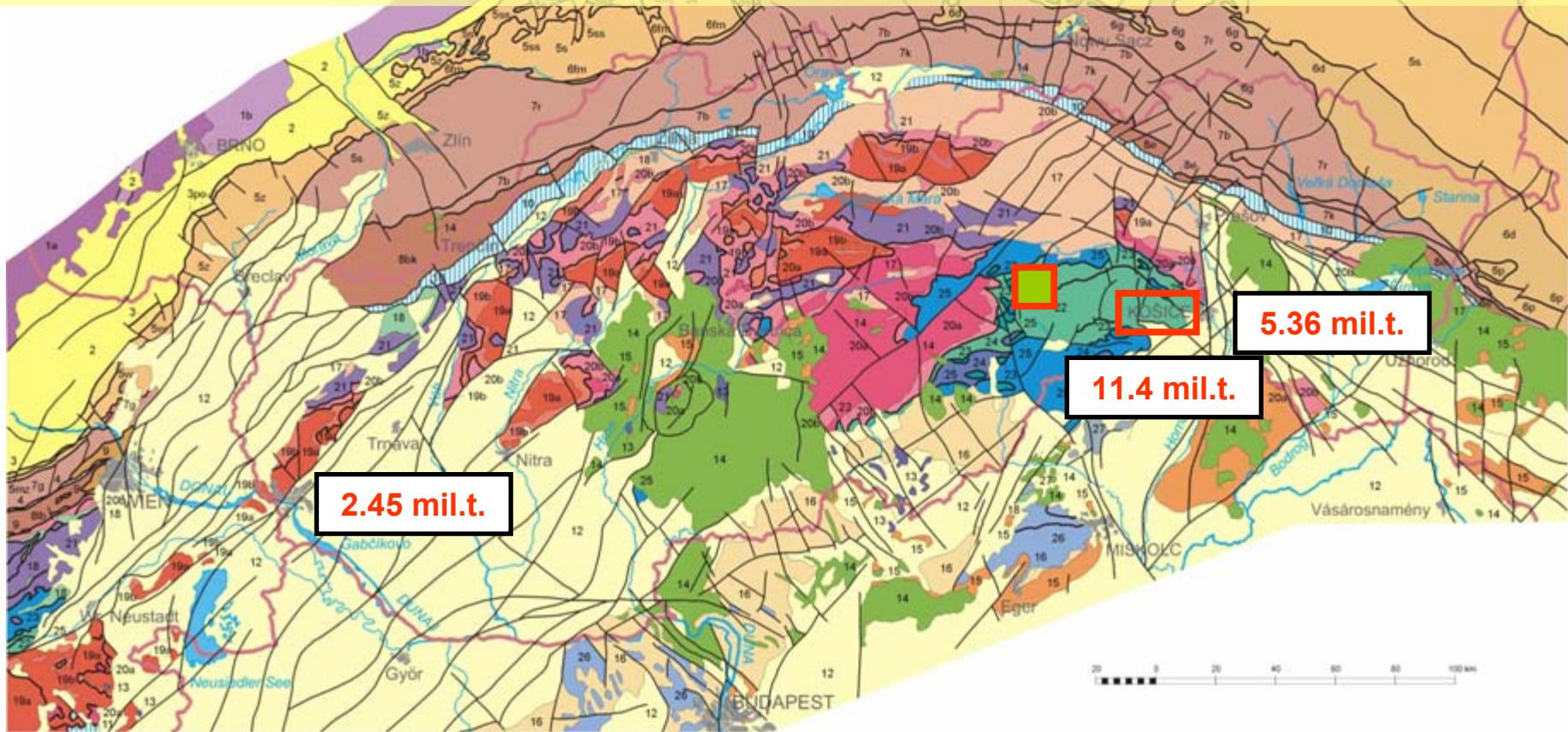
Mineral sequestration

2. Results of experiments



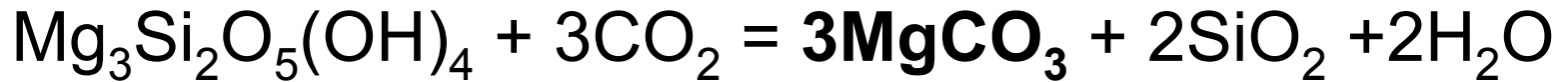


Research in ŠGÚDŠ Bratislava is based on the project “Quantitative parameters of selected geological structures appropriate for CO₂ storage”





The **CO₂ sequestration** by carbonatization at certain p-T conditions:



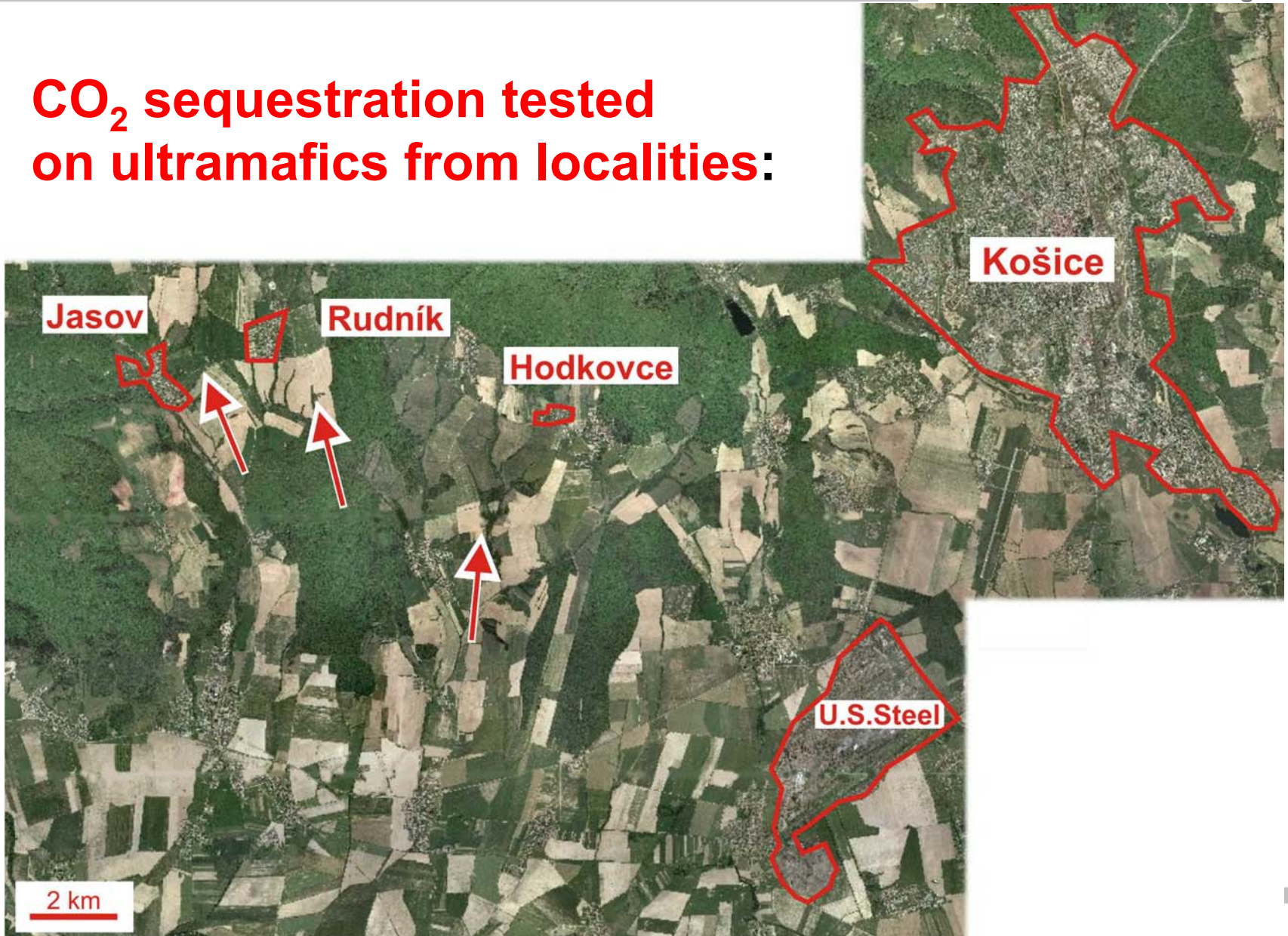
minerals of serpentine group (mainly chrysotile) + CO₂

=> nesquehonite, hydromagnesite => **magnesite**





CO₂ sequestration tested on ultramafics from localities:















Pretreatment of samples: drying, refining, homogenization, quartering and sorting

Homogeneous parts of samples:

X-ray diffraction analyses, chemical analyses, DTA-TGA, microprobe analyses

Hodkovce 2 – crushed stone (granularity beneath 1 mm)



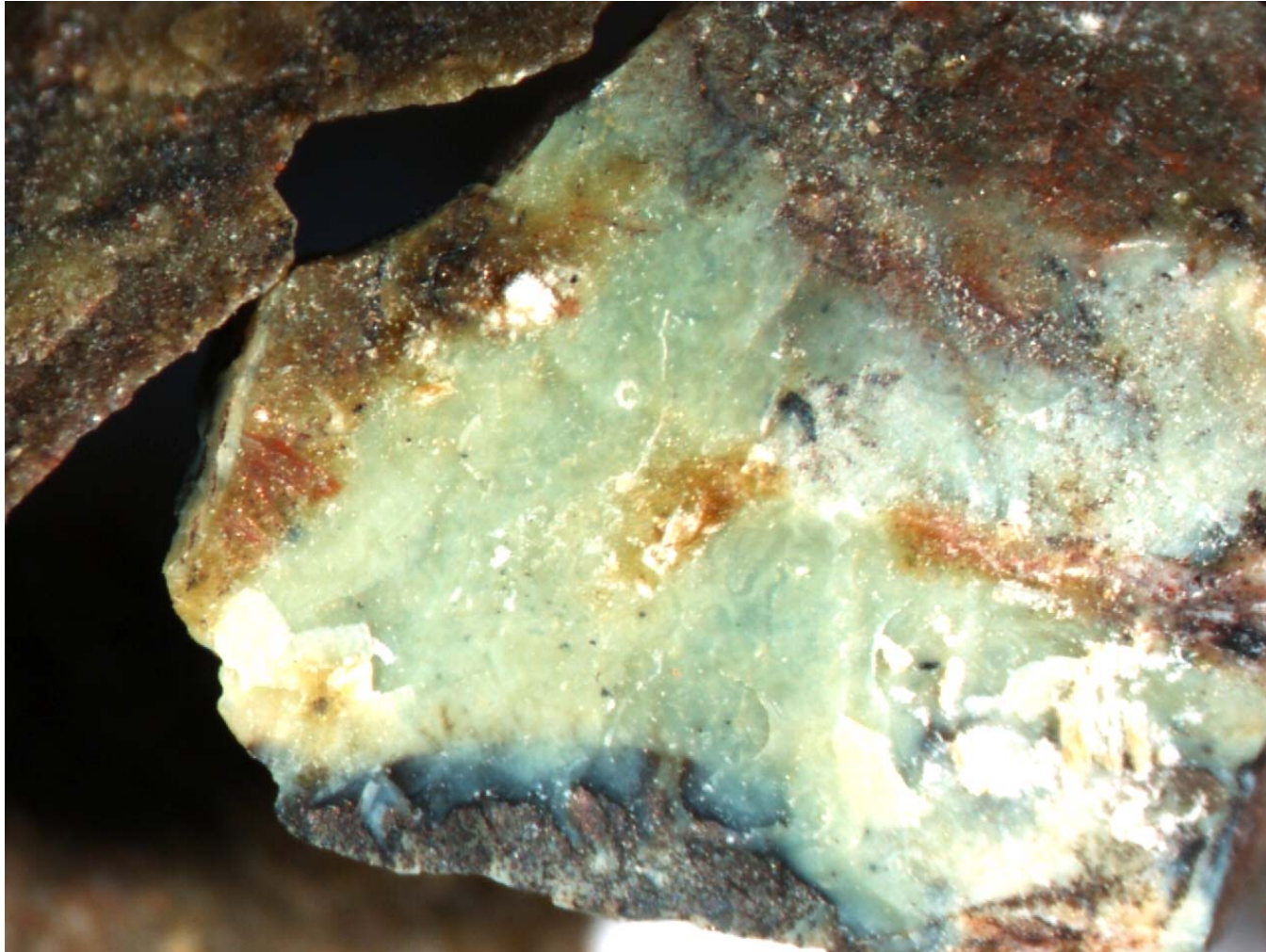


Hodkovce 2 – detail of crushed stone beneath 1 mm





Hodkovce 2 – serpentinite fragment





Hodkovce 2 – crushed stone after thermal processing





Sample from locality HODKOVCE 2

Chemical composition:

| | |
|------------------------------------|-----------|
| SiO₂ | = 40.01 % |
| Al₂O₃ | = 0.77 % |
| Fe₂O₃ | = 8.04 % |
| FeO | = 0.11 % |
| CaO | = 0.24 % |
| MgO | = 36.73 % |
| TiO₂ | = 0.05 % |
| Cr₂O₃ | = 0.334 % |
| MnO | = 0.07 % |
| Na₂O | = 0.01 % |
| K₂O | = 0.02 % |
| P₂O₅ | = 0.01 % |
| Loss.ign. | = 13.44 % |

Mineral composition:

| | |
|------------------------------|-----------|
| Serpentine minerals | = 80.3 % |
| olivine + pyroxene | = 9.9 % |
| magnetite (maghemite) | = 8.9 % |
| calcite | = 0.4 % |
| chromite | = 0.5 % |
| Sum | = 100.0 % |



Pressure, temperature and time constraints of reactions aimed to formation of new solid mineral forms by means of rocks from studied localities and gaseous CO₂:

| | |
|--------------------------------|------------------------|
| Pressure CO₂ | = 0,1 - 0,3 MPa |
| Temperature | = 22 - 200 °C |
| Reaction time | = 5 - 20 hours |
| Crystallization time | = 4 - 24 hodín |



Results of reactions → products with solid chemical bounds of CO₂ on:

□ **solid, transitional phases:**

- amorphous phase of **Mg – Si**
- amorphous phase of **Si**

□ **solid, new products:**

nesquehonite - $\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2\text{H}_2\text{O}$

hydromagnesite - $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$

barringtonite - $\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$

dypingite - $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$

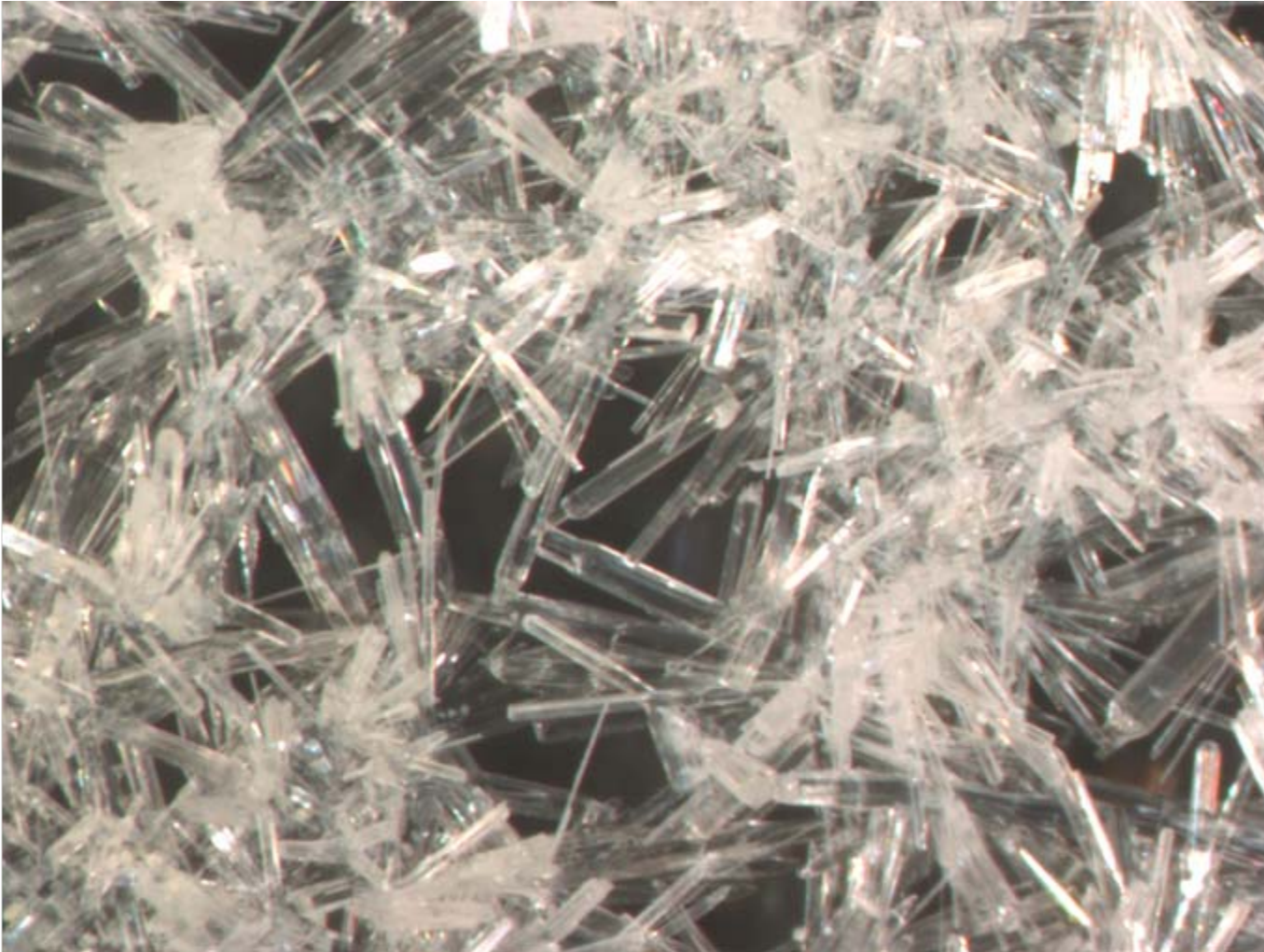


Hodkovce 2 - nesquehonite



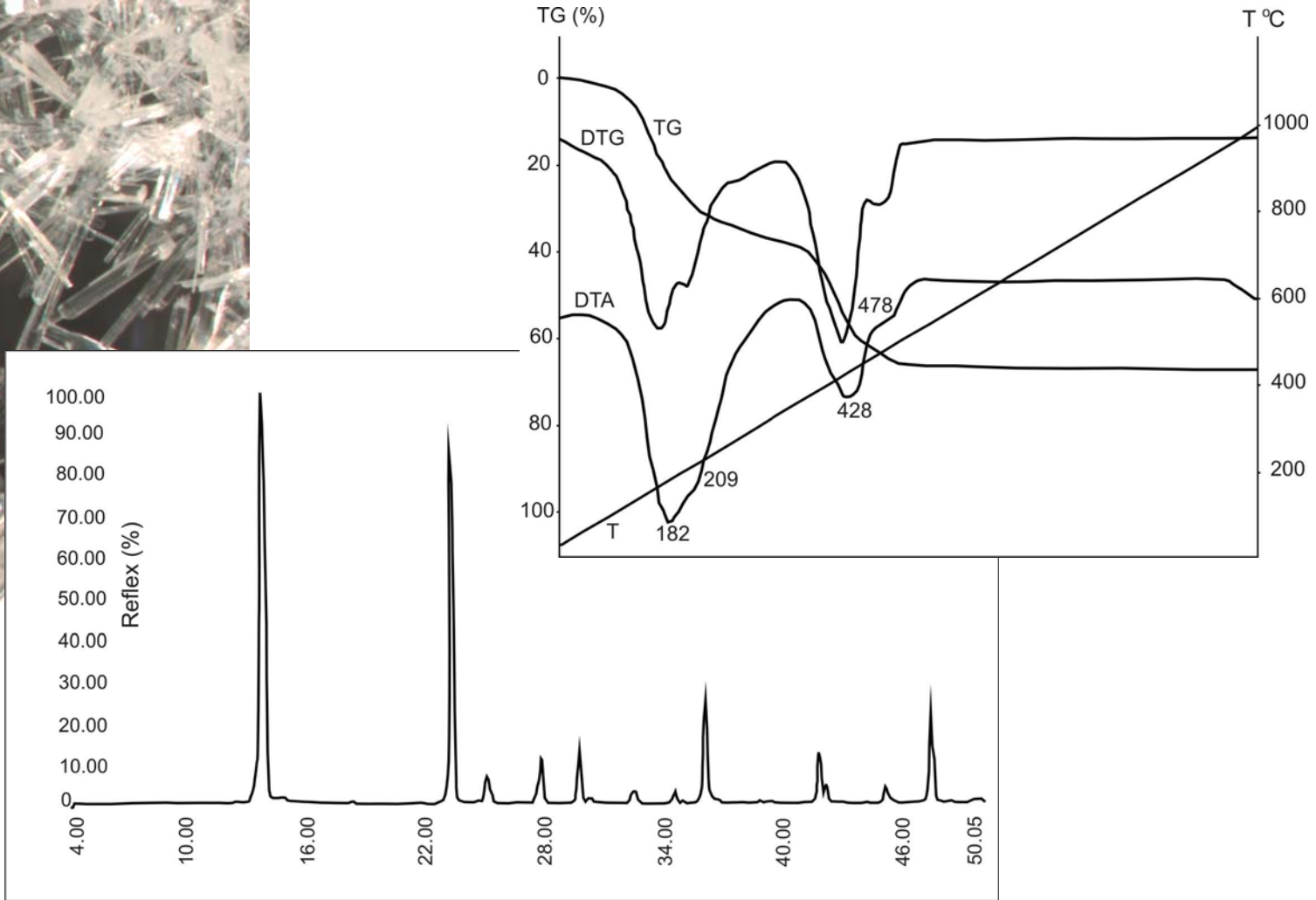
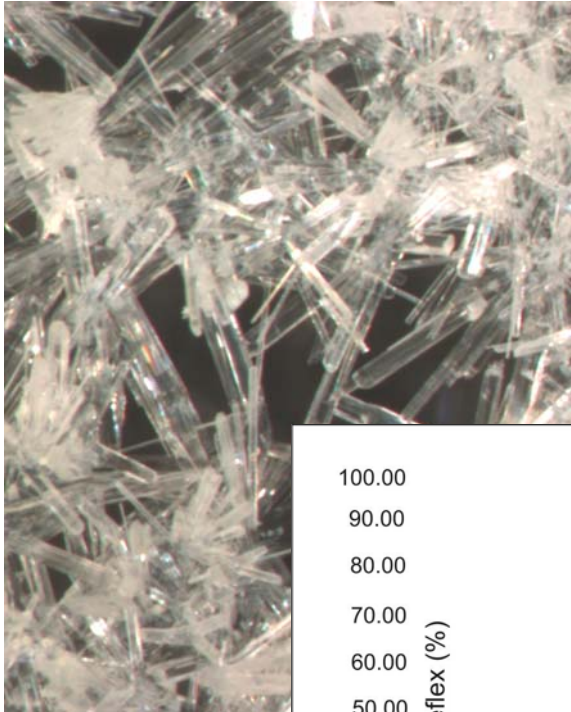


Hodkovce 2 – magnified detail of nesquehonite



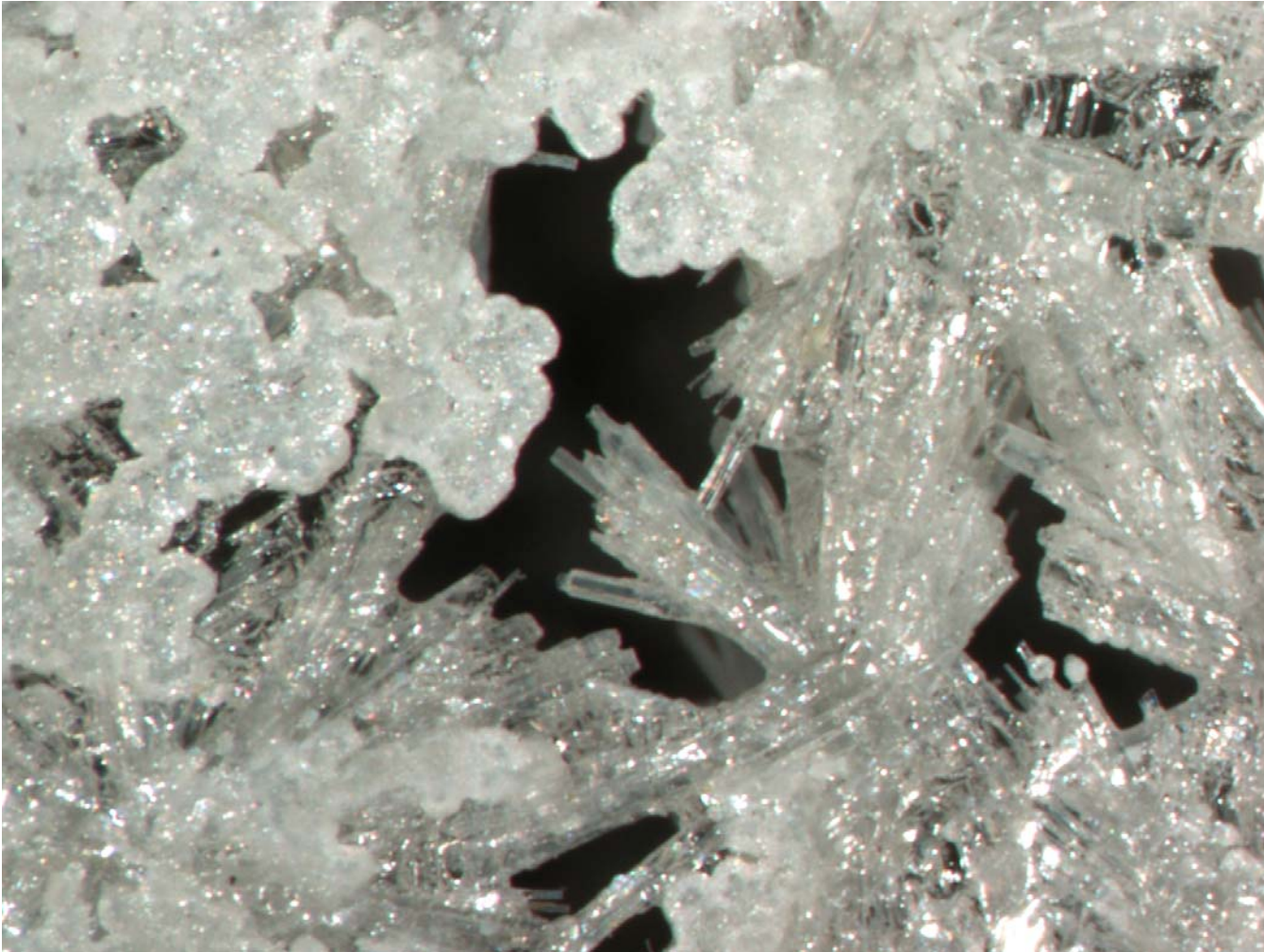


Hodkovce 2 – magnified detail of nesquehonite



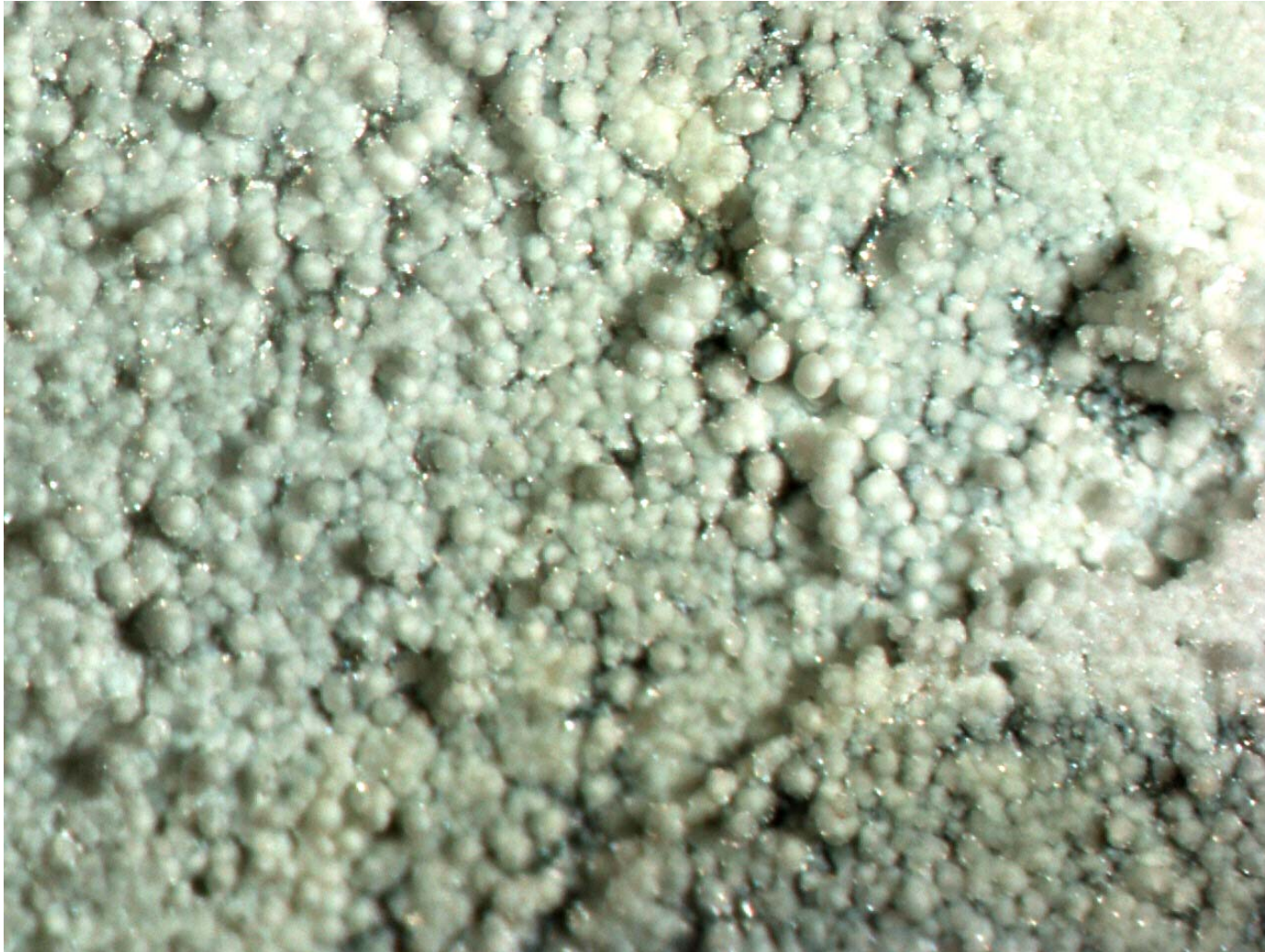


Hodkovce 2 – detail of nesquehonite + hydromagnesite



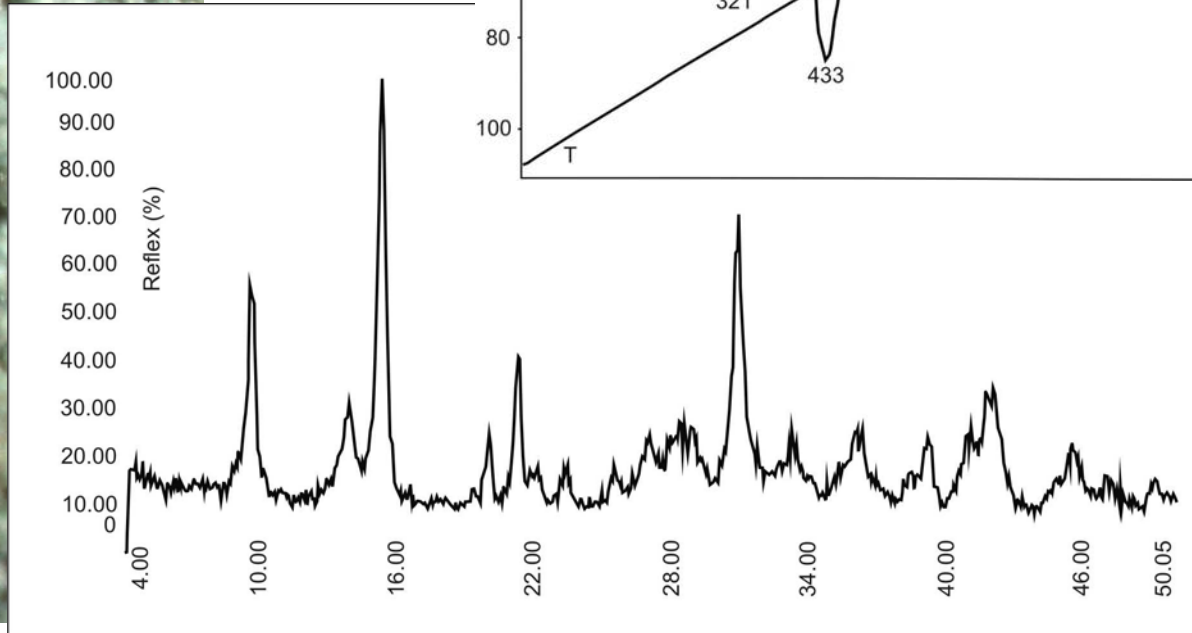
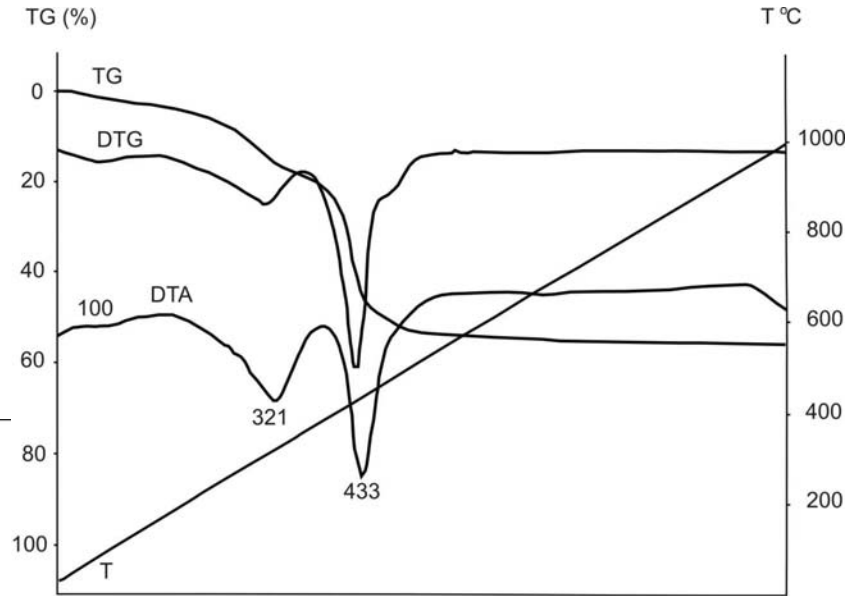
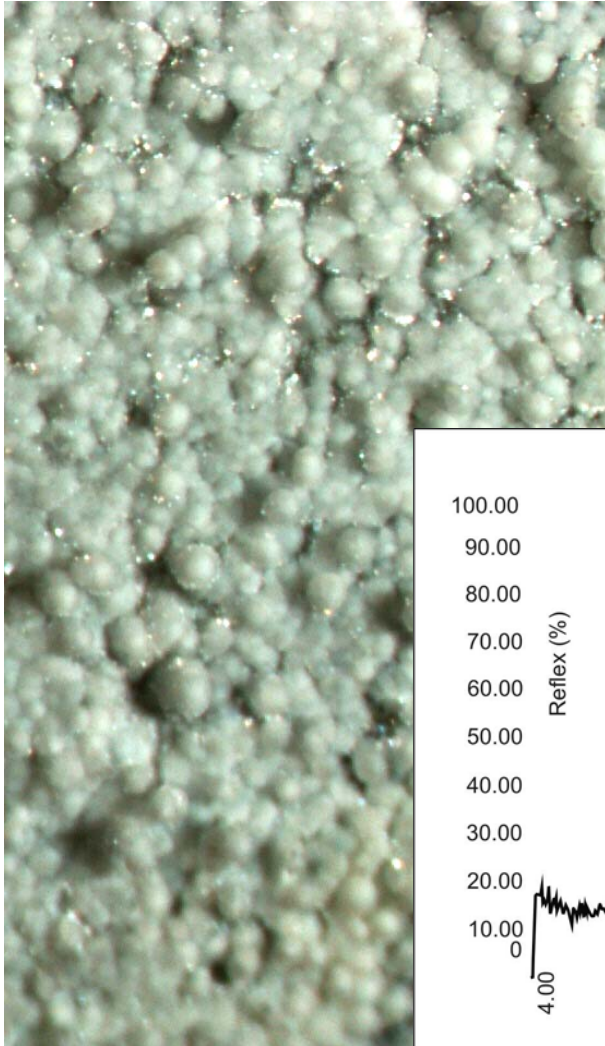


Hodkovce 2 - hydromagnesite





Hodkovce 2 - hydromagnesite





Jasov 1 - nesquehonite





Jasov 1 – detail of nesquehonite



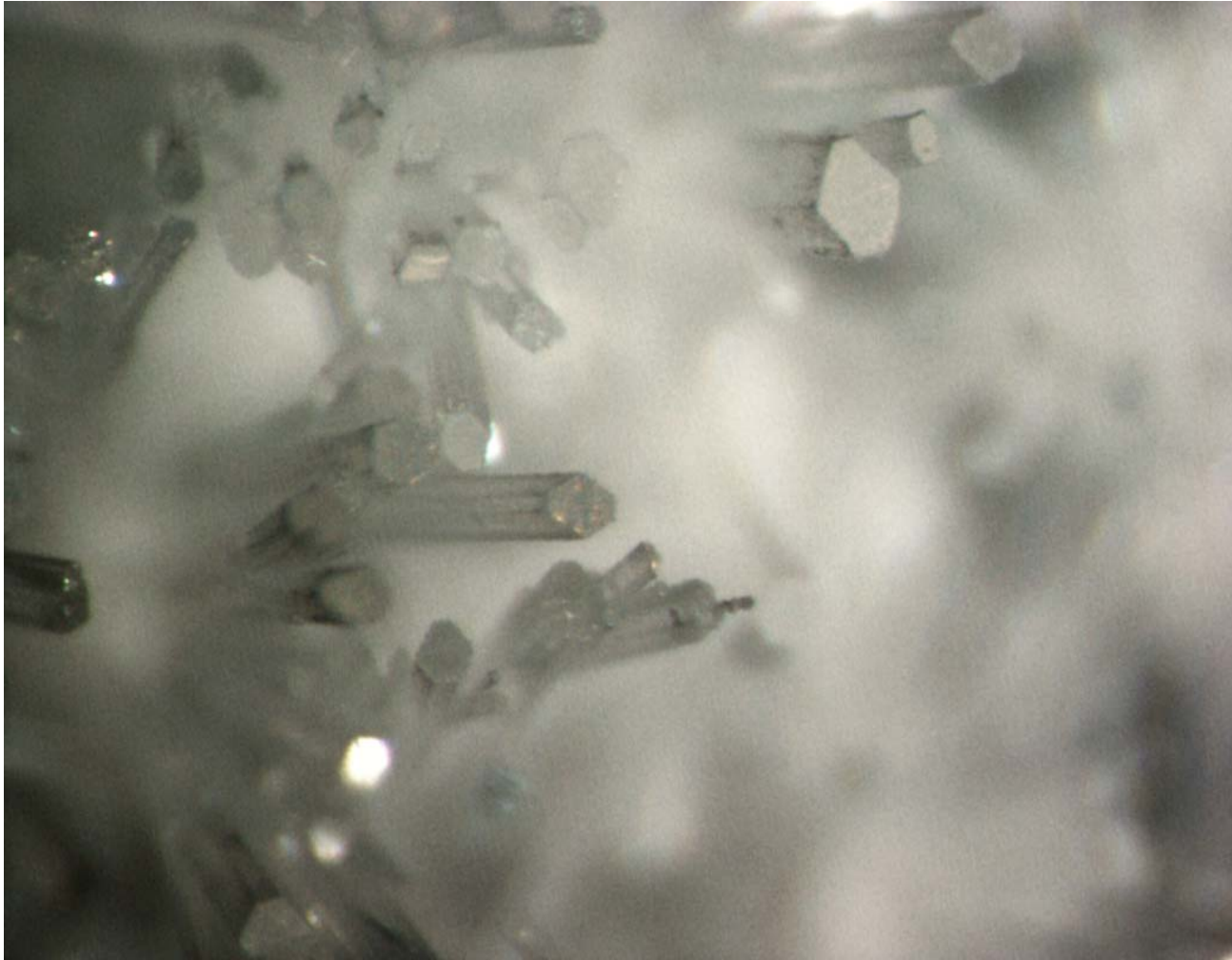


Rudník 2 – detail of nesquehonite





Rudník 2 – detail of nesquehonite





Rudník 2 – detail of nesquehonite + hydromagnesite





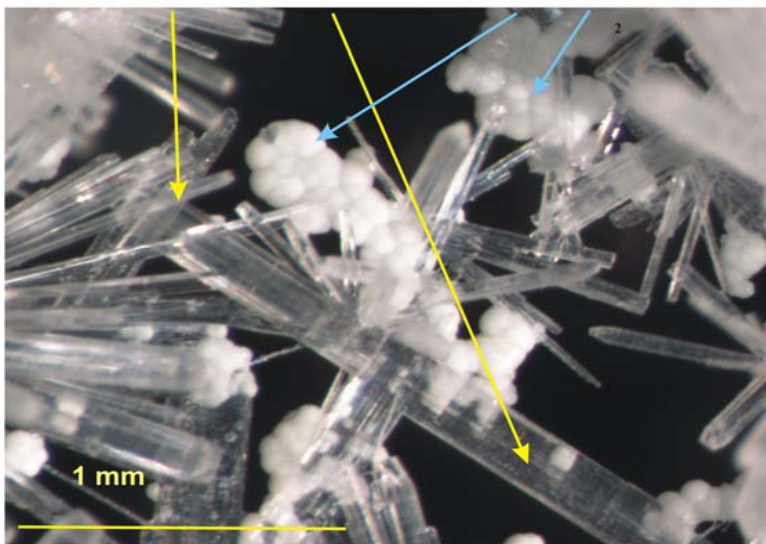
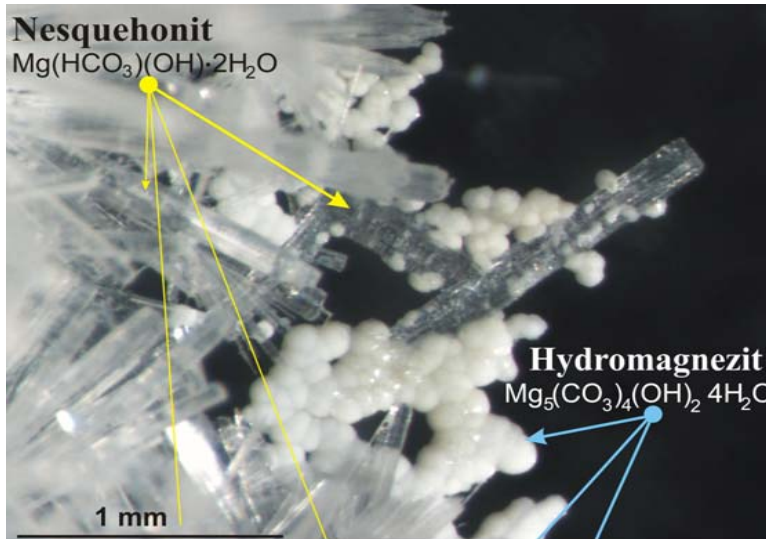
Komárovce 1-11 - nesquehonite





Komárovce 1-11 - detail of nesquehonite





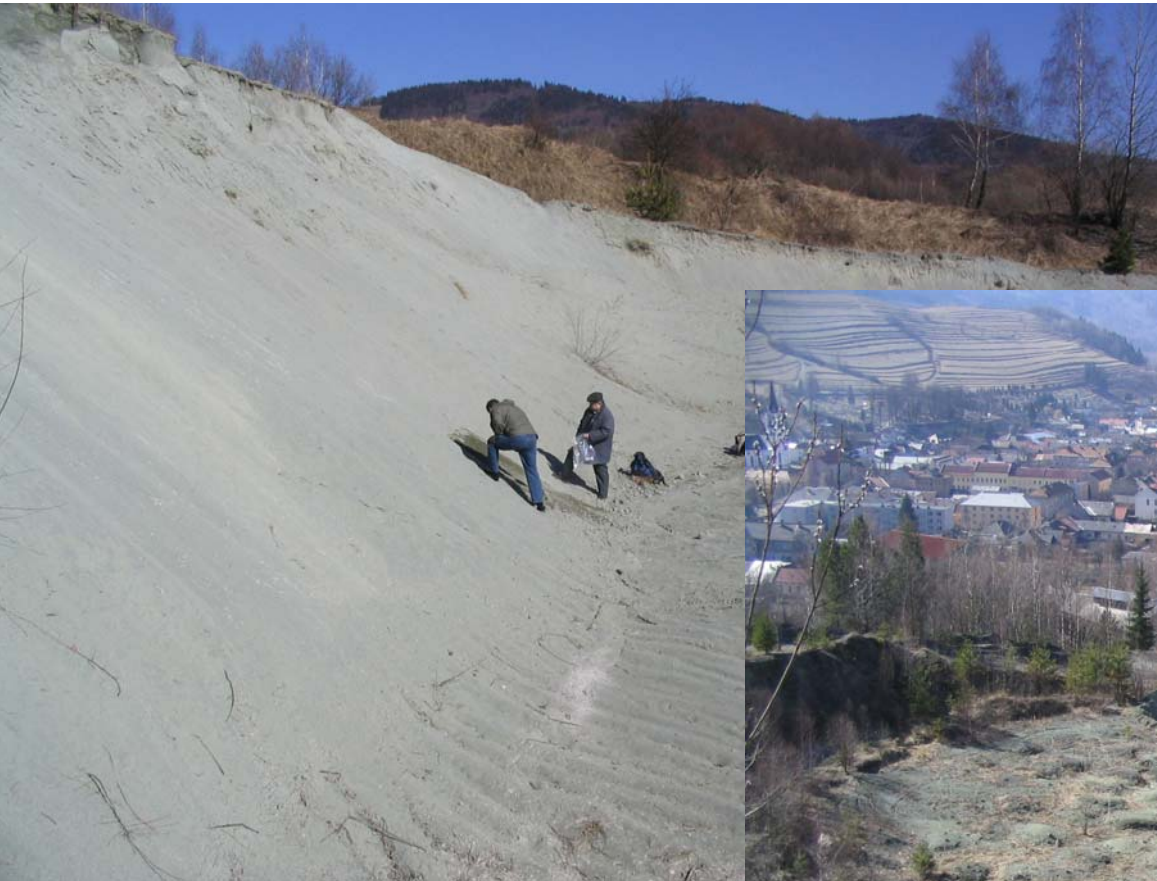
Rudník 2 – nesquehonite and hydromagnesite

Nesquehonit a hydromagnezit, synteticky pripravené minerály pôsobením CO₂ na serpentinit z lokality Rudník. Vzorka RU - 2 - C.



Dobšiná – former exploitation of chrysotile asbestos from ultramafics







Dobšiná – CO₂ sequestration => removal of environmental load





ŠTÁTNY GEOLOGICKÝ ÚSTAV DIONÝZA ŠTÚRA
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NERASTNÉ SUROVINY

EFEKTÍVNEJŠIE a EKOLOGICKEJŠIE

TECHNOLÓGICKÝ VÝSKUM A ÚPRAVA NERASTNÝCH SUROVÍN VÝSKUM V OBLASTI OCHRANY A TVORBY ŽIVOTNÉHO PROSTREDIA

EFektívnejšie a ekologickejšie

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EKOSORBENTY

POSTUPY TECHNOLOGICKÉHO A MINERALOGICKÉHO VÝSKUMU

UKÁŽKA LABORATÓRIÍ

REFERENCIE



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May the workshop CO₂ Capture and Storage starts **new and vivid collaboration of scientists leading to final goal – protecting the Earth against climate changes**