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Preliminary results of the Slovakian national project regarding carbon dioxide storage in underground spaces

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Abstract

The Slovak republic territory in spite of its extremely complicated geological pattern affords some possibilities for potential storage of carbon dioxide. The aim of the Slovakian National project "Quantitative parameters selected geological structures suitable for CO_2 storage" is to find convenient places for this purpose in regional aquifers, and depleted hydrocarbon deposits. Besides, of these geological rock complexes – mostly ultramafic rocks - have been investigated for purposes of mineral carbonation of CO_2. The first attempt about fate of CO2 in brine (regional aquifer) has been modelled from geochemical point of view.. From the preliminary results of the all above - mentioned options is obvious that for the process of the practical activation of CCS technologies many collisions with hydrogeological, geothermal and land use planning activities and regulations will be necessary to solve.

Keywords: the Slovak Republic, saline aquifers, hydrocarbon deposits, mineral sequestration, geochemical modelling

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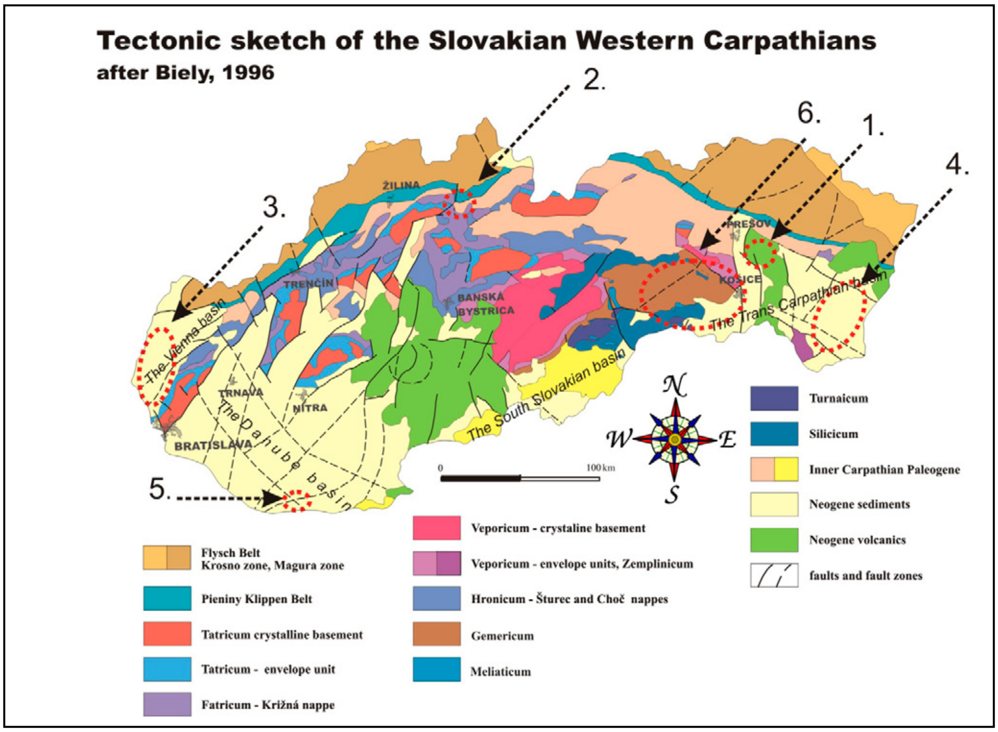
1. Introduction

The geological pattern of the Wester Carpathians developed on the Slovak Republic territory is variegated and complicated. The age of rocks is from the Early Paleozoic to the Quaternary, common is metamorphose (from the green schists to amphibolite facies) and the tectonic development with production of nappes and faults was modelled the territory during the Hercynian and Alpine orogenesis [1]. Around 26 % of the territory is suitable for looking for of resources of geothermal energy. In spite of above mentioned issues that are mostly unfavourable for CO2 storage purpose, certain geological complexes have been selected as the suitable environment for this purposes. On the base of the EU project results CASTOR and GEOCAPACITY was recognise, that possibility for storage are in the Neogene basins (Miocene units), depleted hydrocarbon deposits that are located in the same geological environment. Coal seams was excluded from the evaluation due to unfavourable condition for the targeted purpose.

The national Slovakian project regarding CO_2 storage represents resumption in these activities, initiated in the framework of EU projects. Due to fact, that the Western Carpathians mountain-chain comprises of many occurrences of ultramafic bodies which are integrate into Meliaticum Unit. Geochemical and petrographic characteristic of these rocks indicate evidences of continental rifting volcanism followed by spreading and formation of oceanic crust of Triassic Meliata - Hallstatt basin. Part of oceanic crust was exhumed during middle Jurassic subduction on occur in the mélange complex in the southern part of Gemericum. Relics of this activity are developed in the small forms of serpentine bodies, but several of them possess rather remarkable dimensions and its location is not only in the depth, but also are known even on the surface of the terrain [1]. These bodies have been selected for petrological and technological study from the mineral sequestration point of view.

Fig.1 **The outline of the places under investigation for CO_2 storage purposes** (1. – 6.)



The places under investigation in the contemporary stage are as follows:

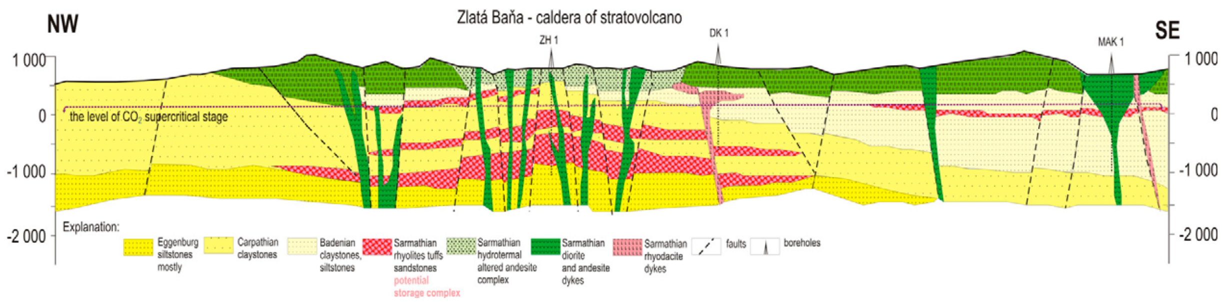
1. Tuffs of rhyolites in the volcano sedimentary environment (Neogene)
2. Aquifers on the base of the Central Carpathians Paleogene and underlying Fatricum unit
3. Depleted hydrocarbon deposits in the Vienna basin
4. Depleted hydrocarbon deposits in the Trans Carpathian basin
5. Regional brine in the Danube basin
6. Ultramafic bodies of Meliaticum unit scattered in the Gemericum unit and its surrounding

2. The description brief of achieved results

2.1 Tuffs of rhyolites in the volcano sedimentary environment (Neogene)

The several horizons of tuffs of rhyolites have been recognize during ore prospecting in the area of the Zlatá Baňa stratovolcano within the Slanské vrchy Mts [3]. The typical (adopted) geological profile is presented in the Fig.2

Fig. 2 The geological cross section through volcano – sedimentary formation; Slánske vrchy (adapted after Kaličiak, et al.1991 [2])



The rhyolites tuffs horizons (lower ones) seemed to be suitable environment for carbon dioxide storage purposes, because possess following positive parameters:

- The relatively high porosity confirmed by the boreholes (about 5%)
- Sufficient thickness as well as areal extension
- Setting in the depths where is supercritical stage of CO_2 definitely attained
- The shape of both lower horizons is in the anticline form
- Pretty well developed thick seal horizons in the hanging wall and in the bedrock (siltstones, claystones)
- Sealing effect is reinforced in the hanging wall by impervious complex of altered andesites in the caldera

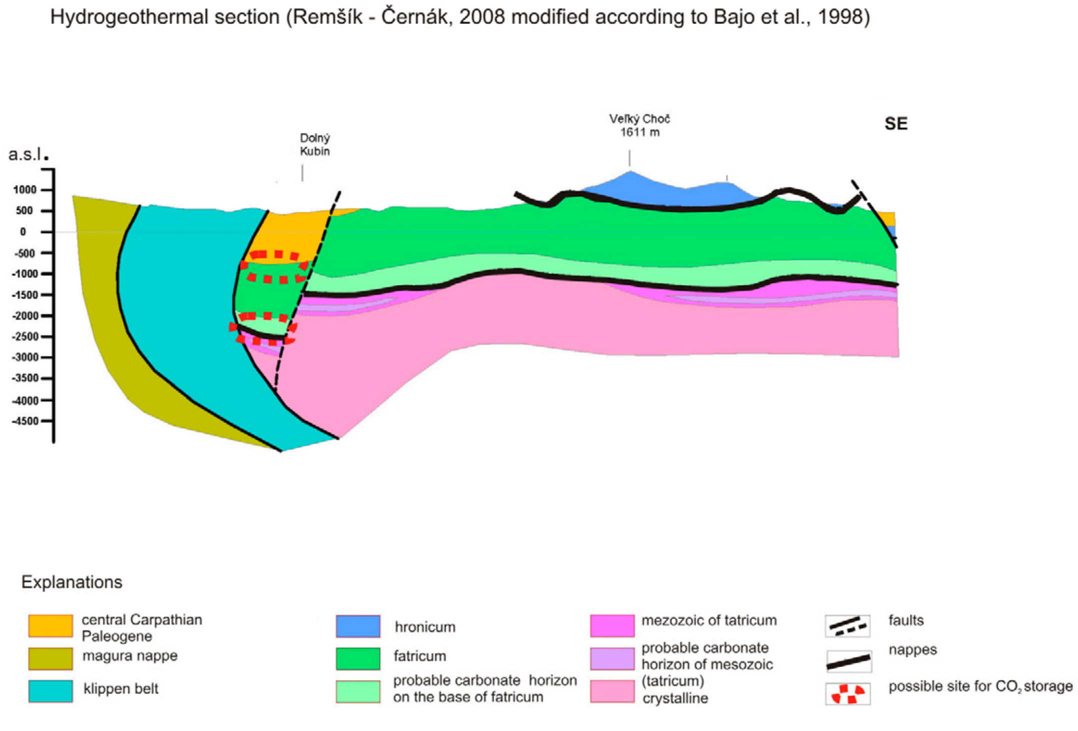
Among negative parameters is possible to assign unknown permeability and missing information about character of younger faults (filling) which partly decomposed stratovolcano body.

The objects account the similar feature as the non structural hydrocarbon trap due to gradual ending out. The estimated theoretical capacity calculated on the base of volumetric approach by the skeptical value of recovery factor (4%) is in the interval between 30 – 60 Mt of CO_2 what could be almost sufficient for period 15 - 20 years for coal thermal power plant with installed capacity 880 MW (2,9 Mt of CO_2 annually) what are data similar to power station Vojany, situated ca. 60km to the SE.

2. Aquifers on the base of the Central Carpathians Paleogene and underlying Fatricum unit

The Central Carpathian Paleogene is in generally considered as the deficit unit for potable water occurrences thanks to lithological composition. On the other hand, its basic unit – borovské complex of beds which consists of prevalently conglomerates is aquifer. It is very high probable that in the depth more than 1 km can high mineralized. In case of occurrence of carbonatic members in its bedrock thus we can expect quite remarkable volume for possible carbon dioxide storage. Such structure is presented on the Fig. 3 where in addition to subjected structure is reasonable to suppose the second storage site in the carbonate development of Fatricum unit. This lover object is potential geothermal structure and therefore its possible utilization is controversial. Anyway the theoretical capacity of the higher structure is about 5 Mt and the lover 15 Mt of CO_2. A targeted investigation for more precisely with technical works would be acceptable.

Fig.3 The storage sites within and bellow Central Carpathian Paleogene [4]



2.3 Depleted hydrocarbon deposits in the Vienna basin

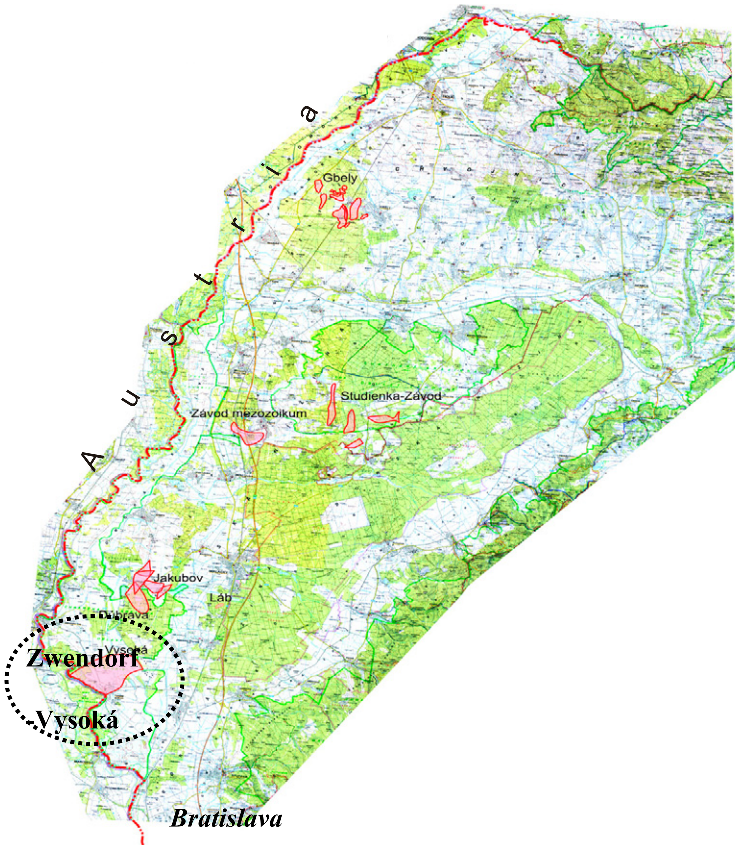
The all available results from the period of several decades of exploitation have been utilized by the detailed evaluation of depleted hydrocarbon deposits.

The capacity **G** was calculated according to formula:

(1) $G_{CO2} = Q_{CH} * B_i * \rho$ where Q_{CH} = exploited volume of hydrocarbons registered on the surface (m^3); B_i = the formation factor; ρ = the CO_2 P,T condition within deposit object

The every object has treated the formular, where are recorded general data about deposit, prospecting history and exploitation, reserves and actual exploitation, primary and actual P and T condition, geological and mining data about colector horizon(s), and overbunden, and chemical properties of hydrocarbons as well. The final evaluation of the objects have been made on the base of their suitability, reliability of verification and description, conflict of interest with other mining activites and threats that may be originated during long time utilization of the structure.

Fig.4 The Vienna basin - the outline of hydrocarbons deposits processed for CO2 storage purposes



The 10 deposits were processed (20 deposits objects) and in term of above mentioned formula the aggregate capacity = 12 Mt has been calculated (besides of Vysoká - Zwendorf deposit).

The Vysoká – Zwendorf gas deposit is located exactly on the frontier between Slovakia and Austria. The deposit is abandoned from the Slovakian side and the exploitation at the Austrian part is almost before ending. The exact data are missing, but according to approximate estimation of gas reserves is possible to store here almost 100 Mt of CO_2. The distance of this object from the refinery in Slovakia – Slovnaft Bratislava is about 30 km, the refinery in Austria - Schwechat Vienna is 40 km. An international agreement regarding exploitation between former Czechoslovakia and Austria will be necessary to open, if this deposit, which seemed to be very convenient, will be utilized for storage purposes.

2.4 Depleted hydrocarbon deposits in the Trans Carpathian basin

The methodology of treatment was the same as in the previus basin. The 5 deposits were processed (30 deposits objects) and the aggregate capacity was 7, 07 Mt. From this amount is clear that deposits are inadequate from capacity point of view. Only objection is the deposit Ptrukša, where the fault block from the Sarmathian unit possesses the calculated capacity 571,7 kt. An applicability and reliability in term of our classification is average only. With regards to the small capacity this object could be serve as a possible pilot project only.

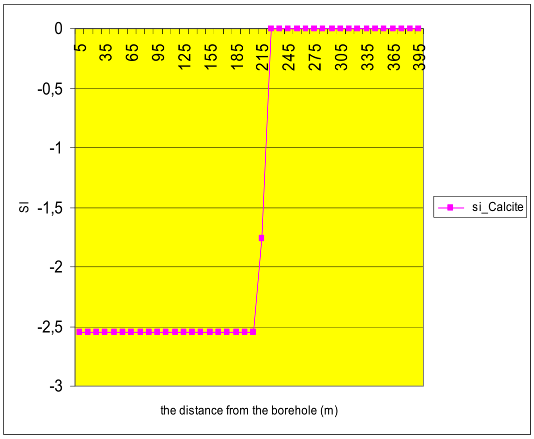
2.5 Regional brine in the Danube basin

The interesting structure is developed in the filling of Danube basin, in its the Early Triassic unit, near village Marcelová. The geochemical modelling with supposed carbon dioxide injection provides following picture:

Tab.: 1

Locality: Marcelová, Danube basin
The depth of collectors: h = 1 760–1 400 m
(limestones, dolomites, alteration of clay shales and sandstones with intercalation of limestones)
TDS=90g/l, The type of water: Na - Cl
Stage phase equilibrium before and after injection of CO_2

	before		after	
Phase	Saturation Index (-CO_2)	CO_2 solulibility	Saturation Index (+CO_2)	CO_2 solulibility
Temperature (°C)	*54*		*54*	
pH	*6,6*		*3,49*	
Pressure of CO2	*0,002 MPa*	*0,0022 mol/kg*	*3,04 MPa*	*0,39 mol/kg*
andradite	7,77		-18,51	
aragonite	0,3		-2,7	
calcite	0,44		-2,55	
dolomite	1,83		-4,16	
$Fe(OH)_3$	1,63		-2,21	
FeOOH	6,41		2,57	
magnezite	-0,08		-3,07	
silica	0,01		0,02	
stroncianite	0,41		-2,59	
talc	0,98		-17,63	



INTERPRETATION

- the brine in the original state is oversaturated by the mineral phases introduced in the Tab. 1
 and will be in the equilibrium with magnesite
- The value of pH traps down after CO_2 rapidly after injection
- Water will become aggressive and will be to dissolve the carbonate mineral phases mainly during which time the indexes of saturation are changed and mineral phases will be undersaturated, what creates increasing of an effective porosity
- The total concentration of CO_2 in brine will be 0,39 mol/kg
- The hydrolytic capacity of the oversaturated brine will be consumed in the distance of ca 230 m from the injection borehole and calcite will get at equilibrium

The locality from this point of view seemed to be promising, but unknown are its trapping geological condition what is important especially with regard to the vicinity of the state boundary with the Hungary.

2.6 Mineral sequestration

This technology was tested in the laboratory conditions (ex situ) using autoclave PARR Instruments (USA). The petrological checking and the petrological computations have been performed with utilizing of microprobe CAMECA SX 100. The mineral carbonatization for CO_2 liquidation was tested using serpentinite from localities Rudník (RU), Hodkovce (HO) and Jasov (JA) in the East Slovakia. The laboratory pilot tests have demonstrated that new, solid and high purity products of mineral carbonatization can be prepared from samples of these localities after their granular and thermic modification at particular P-T conditions with subsequent crystallization of carbonate minerals from filtrates [6].

The new products based on serpentinite were produced in relatively short time of several hours. Originated carbonate minerals – nesquehonite, hydromagnesite, less barringtonite

Pressure, temperature and time constraints of reactions:

Pressure CO2	**= 0.1 - 6.0 MPa**
Temperature	**= 22 - 200 ^{o}C**
Reaction time	**= 5 - 20 hours**
Crystallization time	**= 4 - 24 hours**

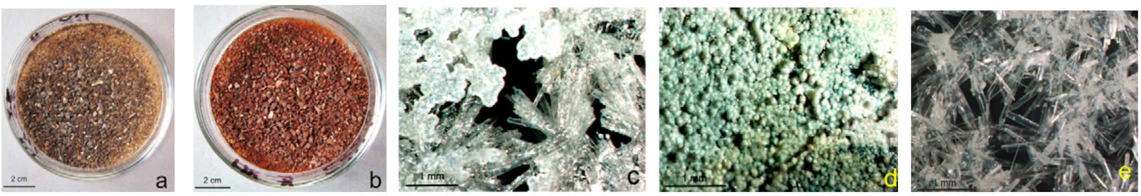
Tab.2 The chemical and mineral parameters of output rocks – carbonates

Chemical compound (wt.%)	RU-1	RU-1	RU-2	RU-2	HO-1	HO-1	HO-2	HO-2	HO-2	JA-1	JA-1
p (MPa) - T (°C) reaction time (hour)	0.3-22 5	0.3-22 5	0.1-22 20	0.1-22 20	0.3-22 5	0.3-22 5	0.3-22 5	0.3-22 5	0.3-22 5	0.1-22 20	0.1-22 20
crystal. time (hour) - cryst. temper. (°C)	24 - 50	4 - 200	24 - 50	4 - 200	24 - 50	4 - 200	24 50	5 160	4 - 200	24 50	4 - 200
SiO_2	0.76	0.99	0.82	1.03	1.35	1.70	0.99	0.84	0.94	1.18	0.94
Al_2O_3	0.08	0.07	0.17	0.07	0.09	0.07	0.16	0.08	0.06	0.14	0.06
$Fe_2O_{3\ total.}$	0.02	0.02	0.03	0.02	0.05	0.05	0.04	0.03	0.02	0.03	0.02
CaO	0.51	1.21	0.63	1.29	0.76	1.37	0.50	0.86	0.93	0.84	1.46
MgO	34.14	42.48	34.90	42.60	34.25	42.54	30.09	42.05	43.14	35.11	42.01
TiO_2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MnO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
K_2O	0.01	0.02	0.01	0.03	0.02	0.03	0.02	0.03	0.04	0.02	0.04
Na_2O	0.06	0.10	0.09	0.13	0.07	0.13	0.13	0.19	0.10	0.13	0.12
P_2O_5	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01
Cr_2O_3	0.27	0.299	0.24	0.362	0.09	0.086	0.039	0.19	0.12	0.12	0.18
CO_2	34.00	35.59	36.43	35.80	33.28	34.92	32.70	35.64	35.97	34.75	35.90
loss by ignition	63.92	54.60	62.66	54.16	63.12	53.77	67.80	55.55	54.33	61.87	54.78

Sample designation	Mineral component (wt.%)				
	nesquehonite	hydromagnesite	calcite	other oxides	Sum of carbonates
RU-1 (50 °C)	97.9		0.9	1.2	98.8
RU-1 (200 °C)		96.3	2.2	1.5	98.5
RU-2 (50 °C)	97.5		1.1	1.4	98.6
RU-2 (200 °C)		96.0	2.3	1.7	98.3
HO-1 (50 °C)	96.9		1.4	1.7	98.3
HO-1 (200 °C)		95.5	2.4	2.1	97.9
HO-2 (50 °C)	97.6		0.9	1.5	98.5
HO-2 (160 °C)		97.1	1.5	1.4	98.6
HO-2 (200 °C)		97.0	1.7	1.3	98.7
JA-1 (50 °C)	96.9		1.5	1.6	98.4
JA-1 (200 °C)		96.0	2.6	1.4	98.6

The formation of new products on the base of serpentinite occurred in relatively short time of several hours. Obtained carbonate minerals are potentially usable in manifold industrial branches as white inorganic infilling into plastics, paints, binding constituents, glues, rubber, paper, etc…

Fig. 5 Mineral sequestration of the samples from the Hodkovce locality

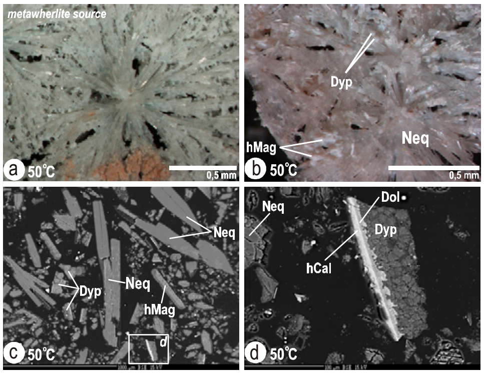


a) input material crushed beneath 1.0 mm; b) thermically elaborated material crushed beneath 1.0 mm;

c) nesquehonite and hydromagnesite (160^{0}C); d) hydromagnesite (200^{0}C) e) nesquehonite (50^{0}C)

The example and conclusion of the petrological research is presented bellow:

Fig 6 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.



According to petrological calculations the ideal weight of CO_2 liquidated in 1 m^3 of metaperidotite, metawehrlite and metawebsterite the sequestered weight of carbon dioxide from 902 kg to 1 264 kg. This volume does not depend neither the temperature condition of artificial carbonatization nor the type of the source rock. The gradual temperature increases from 50^0C through 160^0C to 200^0C 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 50^0C while higher temperatures serve as a suitable environment for carbonates formation [6].

The all known ultramafic bodies which possess remarkable volume will be investigated in the framework of this project.

3. Conclusion

- Possibilities for CO_2 storage in the Slovak Republic are in spite of its complicated geological pattern noticeable (concerning to annual CO_2 production) and variable as well. The theoretical storage potential is approximately for 50 years.
- Similarly as in other countries the biggest potential is in regional aquifers, where is on the other hand lack of reliable knowledge. Moreover many conflicts of interest are probable in the future in this issue due to vital interests connected with potable water sources and geothermal energy utilization
- The depleted hydrocarbons deposits are negligible (besides the one objection) from the capacity point of view and suitable for pilot study only.
- The sphere of mineral sequestration seemed to be promising, because can contribute into raw material policy and into energy sector. There is a great challenge for the future to push this technology into pilot stage.

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