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ÚJV Řež, a. s.

EGU2020-20326

EVALUATION OF CRYSTALLINE ROCK PORE WATER GEOCHEMISTRY IN DGR CONDITIONS

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EGU General Assembly, Web meeting, May 4, 2020

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Presentation outline

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1. **Introduction**
2. **GW Porewater**
3. **Crystalline rocks used for analyses**
4. **Methods used**
   - Laboratory out-leaching
   - High pressure extraction
   - In situ extractiion
   - Modelling
5. **Result comparison**
6. **Conclusions**

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Crystalline rock porewater

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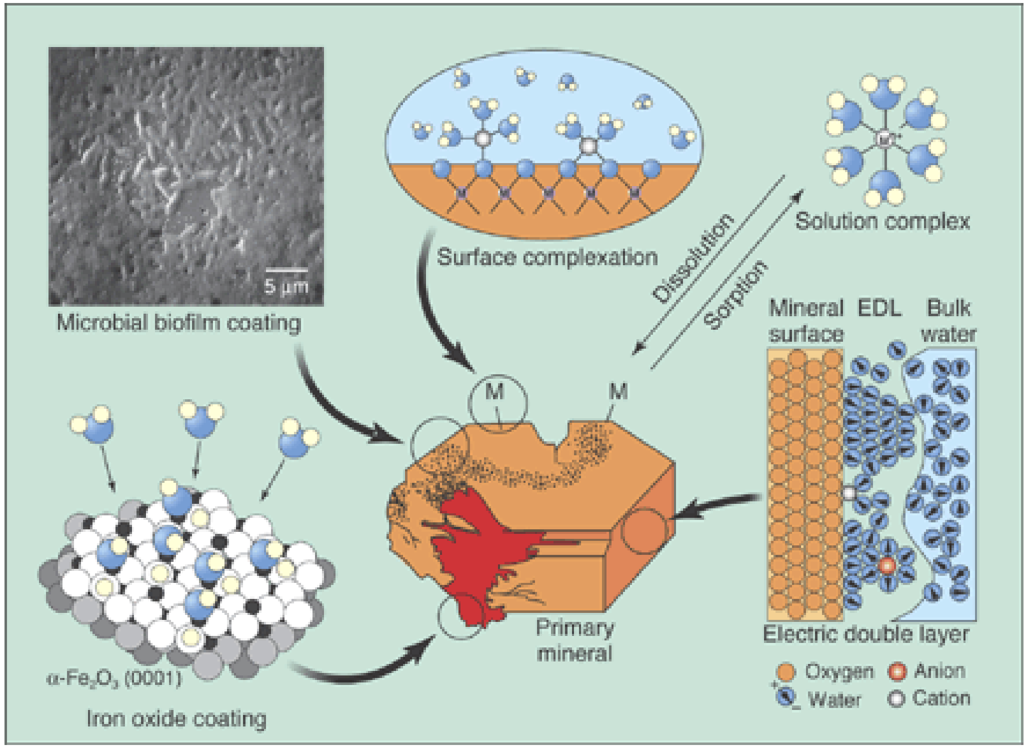
Porewater refers to the water in the connected pore space of the rock matrix that is accessible for diffusion-dominated interaction with groundwater circulating in nearby (micro)fractures.



Brown (2001): Science 294, 67-69

Main reactions (and species):

- biotite dissolution (K, Mg, Fe, F), plagioklasu (Ca, Na),
- K-feldspar dissolution (K, Na),
- calcite dissolution (Ca),
- pyrite dissolution (Fe, SO_4),
- fluorite dissolution (F, Ca)
- magnetite dissolution (Fe).

Importance: RN form, speciation, retention, precipitation

Crystalline pore water determination

- Outleaching
  (Eichinger et al. 2008, 2010; Waber and Smellie et al. 2008)
- Diffusion experiments
  (Smellie et al. 2003)
- High pressure extraction
  (Smellie et al. 2003)

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Crystalline rock porosity

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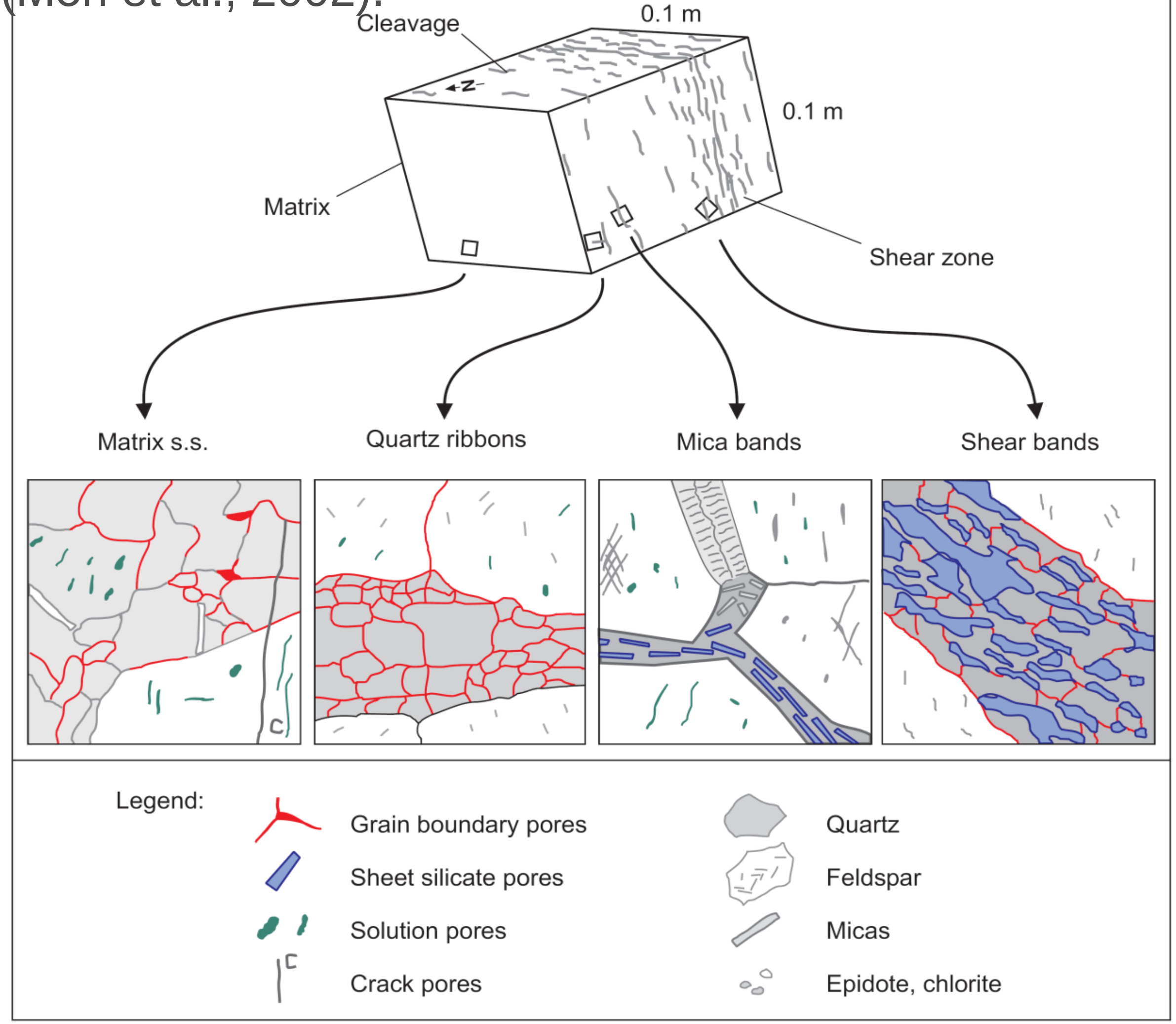
(Möri et al., 2002).



Porosity values in crystalline rock:

Generally below 1 %

CZ crystalline rocks: ~ 0,6%

20 cm of Ø 50mm core = <u>2,36 ml of solution total</u>

BUKOV URF (CZ, SURAO) – Rožná mine

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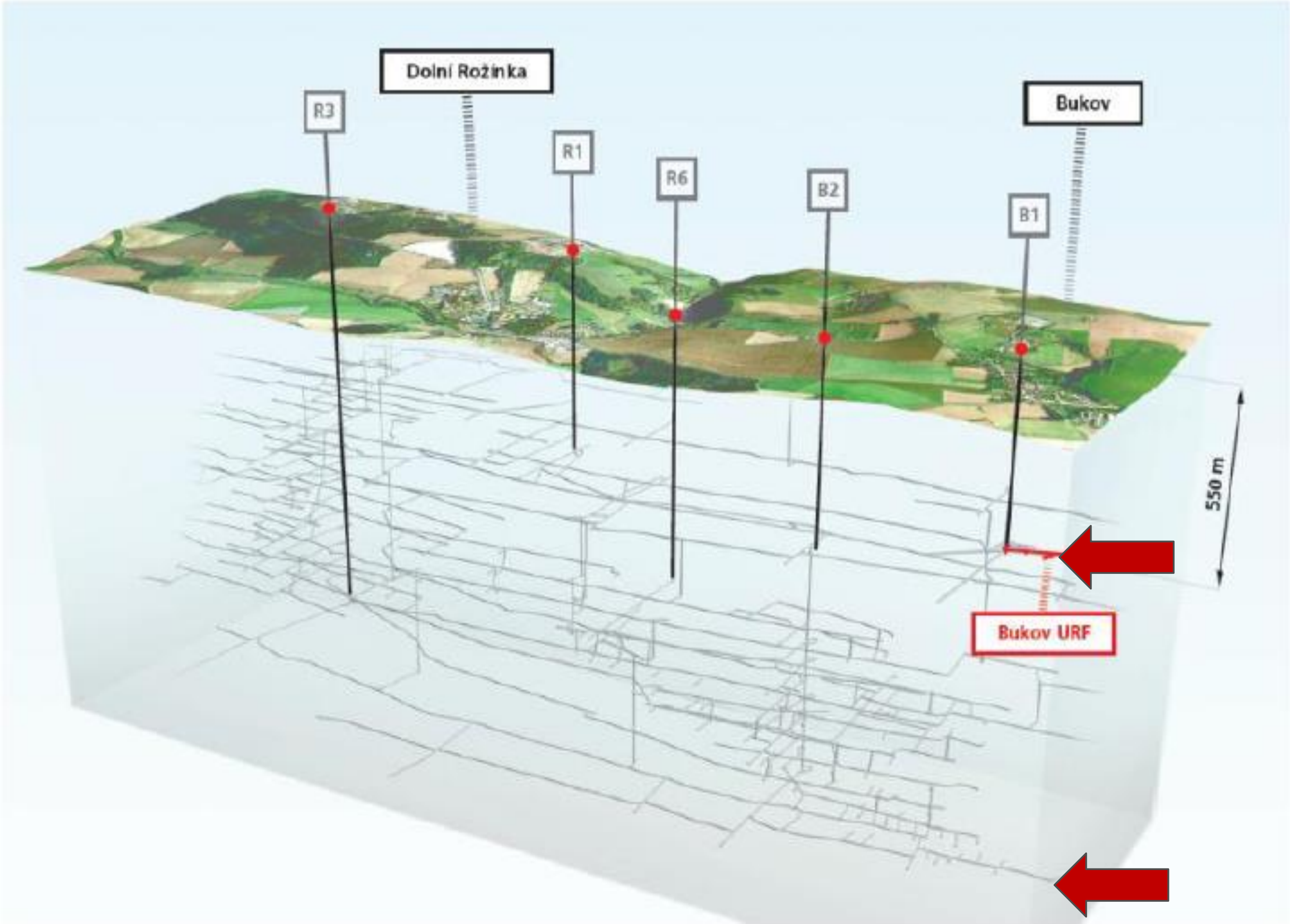
Source: SURAO

BUKOV URF (SURAO)



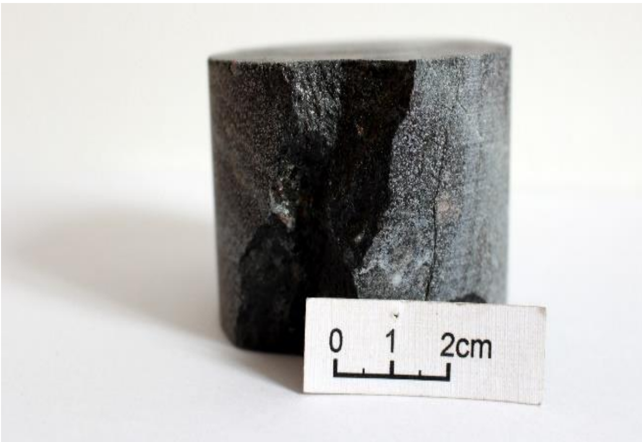
(SURAO, J. Smutek, Waste forum, 2018)

Project is funded by SURAO

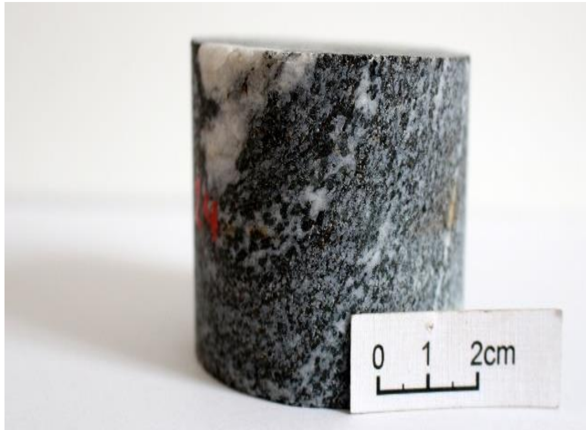
Rock samples

- **borehole BGS12-H** (amphibole-biotite gneiss with garnet) – the 12th horizon; - 500 m
- **borehole BGS24-I** (biotitic amphibolite) – the 24th hor., -1 200m
- thorough collecting and transfer to lab
- gravimetric water content (%), porosity, bulk density, specific density, silicate analyzes
- **Porosity ~ 0,3 %**

The rock samples of drill cores were kept under the vacuum



Amphibole – biotite gneisss with garnet (BGS 12 – H).



Biotite amphibolite (BGS 24 – I).

Laboratory out leaching

- Samples (200 x 60 mm) installed in diffusion cells with approx. 90 ml of ultrapure water (DW).
- In the surrounding reservoir Cl^- (representing conservative anions), SO_4^{2-}, F^-, NO_2^- and NO_3^- monitored.
- all major anions and cations were analyzed by means of AAS and ICP-OES, HPLC

Presumption

- **Pore water in pore space is not disturbed by drilling water**
- **Diffusion only toward ultrapure distilled water in surrounding reseroirs**

Diffusion cells 1 – 4, stirring of the surrounding solutions before sampling

Cl diffusion out of the rock samples

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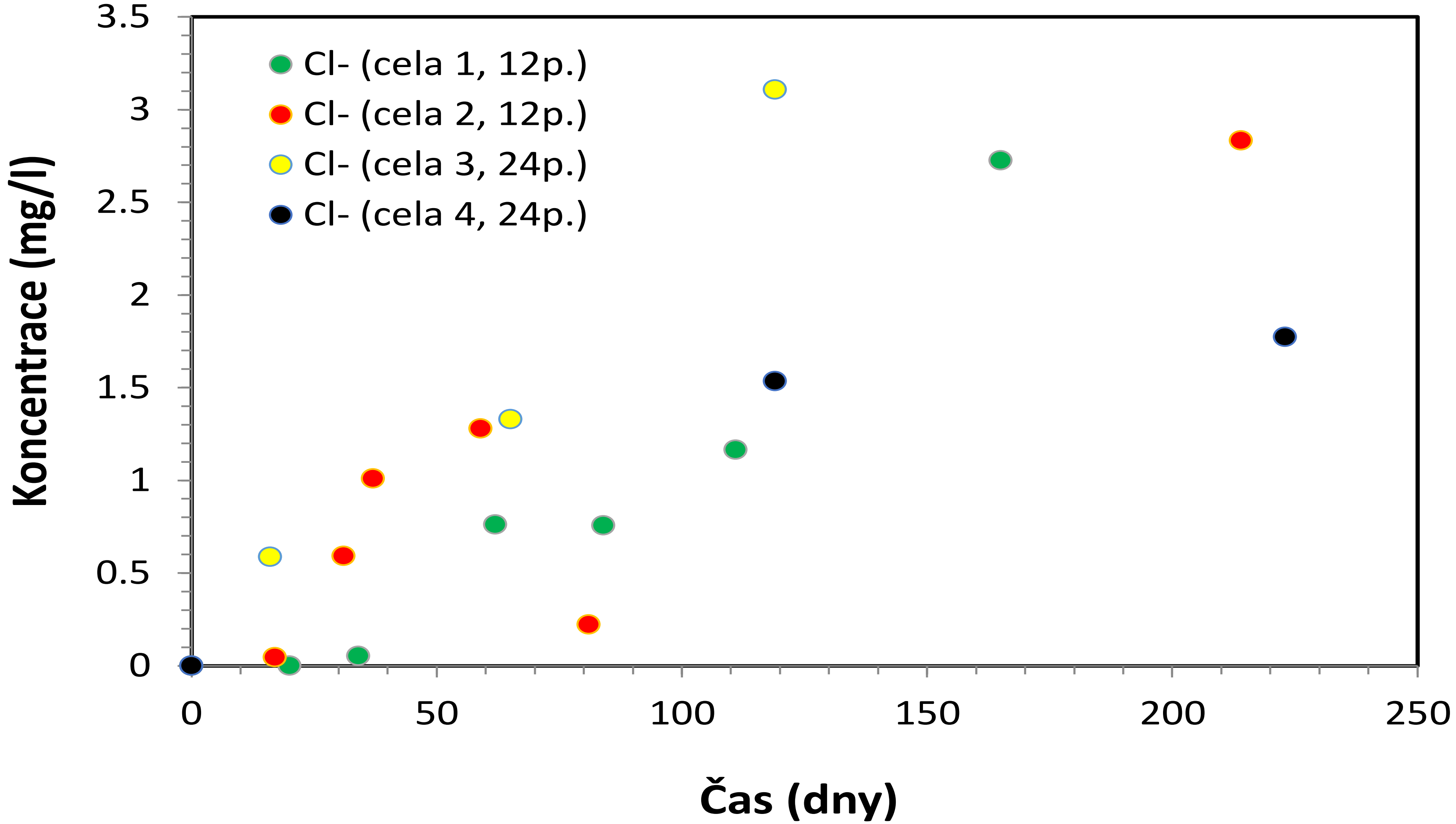

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High pressure extraction

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Rock sample BGS12-H of 60 mm length, Ø 60 mm

- Installed into the permeameter
- 10 MPa pressure applied as a background
- 3 Mpa presure of N_2 applied on the sample
- No water appeared outletting the sample…

Not appropriate method for low porosity samples

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In-situ pore water extraction in Bukov URF

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- A double packer with a sampling interval (20 cm, +20 cm) was manufactured for in-situ pore water sampling with two sampling inlets for either suction or pressurisation of the sampling interval (PEEK)

- The in-situ sampling intervals were placed in the borehole intact parts, in the vicinity of drill core sections sampled for laboratory experiments.

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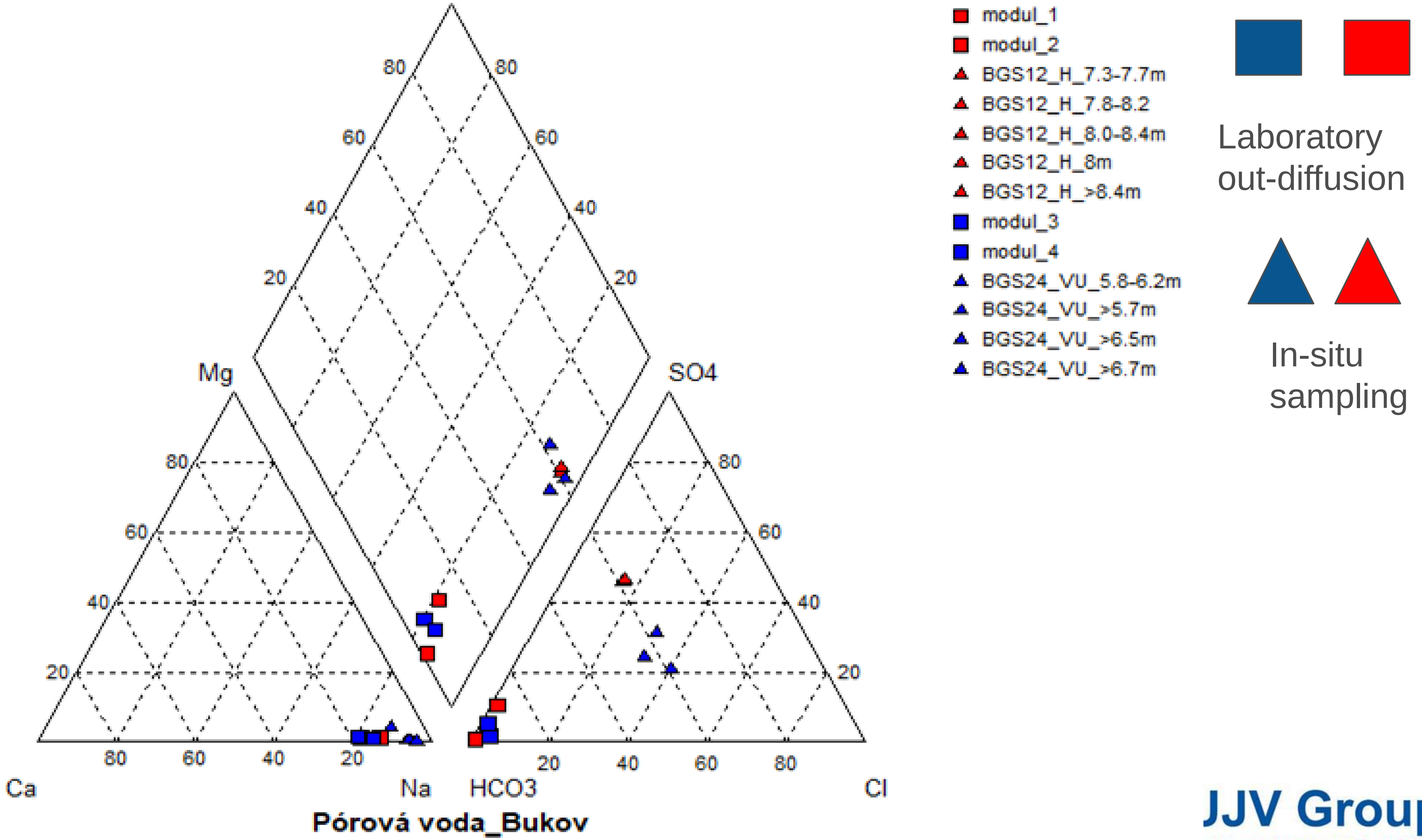
Sampling

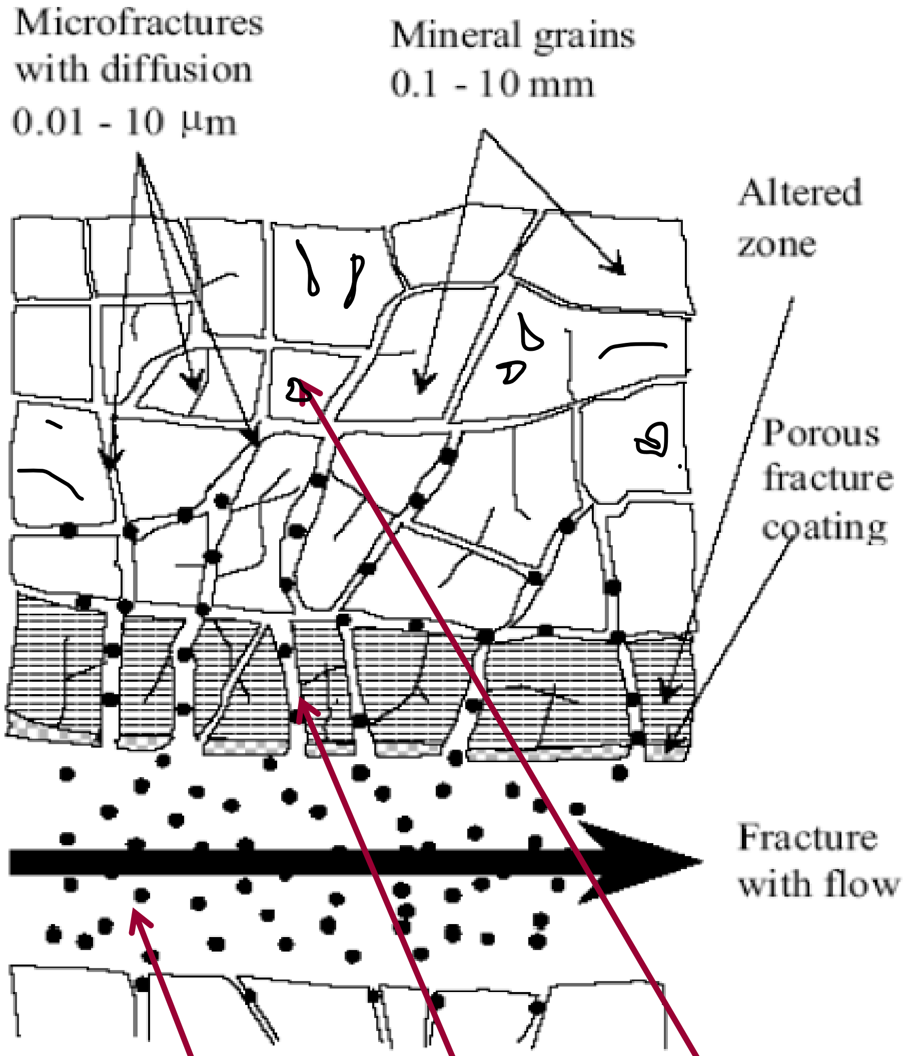
- **BGS12** (12th horizon) – original borehole; undisturbed part in the depth of 7.3 – 7.8 m; 20 hours, 27 ml of solution; evaccuation

- **BGS24-VU** (24th horizon) – vertical borehole, undisturbed part in the depth of 5.8 – 6.2 m; 6 days, 77 ml of solution; evaccuation

Comparison of out diffusion experiments with in-situ sampling



Modelling: GW in contact with rock constituents



$$\varepsilon = \varepsilon_f + \varepsilon_t + \varepsilon_r$$

https://wgnhs.uwex.edu/maps-data/data/rock-properties/understanding-porosity-density/

- ε *total porosity*
- ε_t *flow porosity (advection)*
- ε_t *effective porosity (diffusion)*
- ε_r *residual porosity (dead end pores)*

Modelling

- PHREEQC
- Step by step equilibration of rock forming minerals with groundwater at the horizon
- Presumption:
  - GW enters the pore space from the fracture
  - Rock minerals have different reactivity
    1. **Minerals with high surface** (chlorite, calcite)
    2. **Biotite**
    3. **Other alumosilicates**

XRD analyses of the analysed rocks

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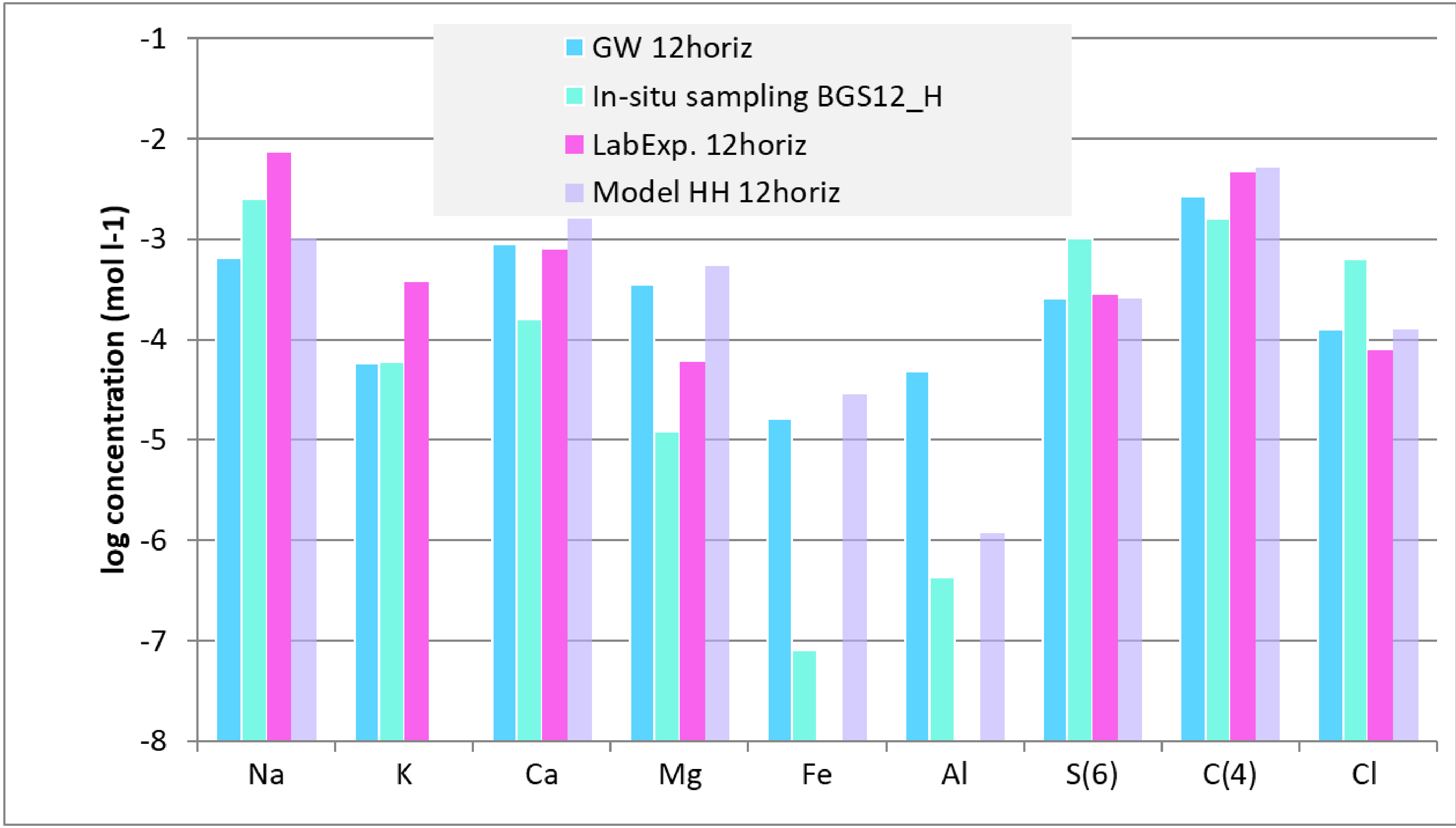
Sample	Minerals		Abundance (%)
BGS 12-H WR 12th level	**Amphibole**	$Ca_2(Mg,Fe2+,Al)_5(Si,Al)8O_{22}(OH)_2$	25
	Plagioclase	$Ca(Al_2Si_2O_8)$ albite	37,5
	K-feldspar	$KAlSi_3O_8$	2
	Quartz		18,5
	Biotite	$K(Mg,Fe^{2+})_3(Si_3Al)O_{10}(OH,F)_2$	10,5
	Chlorite	$Mg_5Al(AlSi_3O_{10})(OH)_8$	3
	Calcite	$CaCO_3$	1
	Garnet		2,5
BGS 24-I WR 24th level	**Amphibole**	$Ca_2(Mg,Fe2+,Al)_5(Si,Al)8O_{22}(OH)_2$	31,5
	Plagioclase	$Ca(Al_2Si_2O_8)$ albite	39
	K-feldspar	$KAlSi_3O_8$	1
	Quartz		18
	Biotite	$K(Mg,Fe^{2+})_3(Si_3Al)O_{10}(OH,F)_2$	7
	Chlorite	$Mg_5Al(AlSi_3O_{10})(OH)_8$	3
	Calcite	$CaCO_3$	0,5

GWs for equilibration

Type	pH	Concentration (mg l^{-1})										Type	log P_{CO2}
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	$SiO_2(aq)$	Al^{3+}	Fe^{2+}		
SGW2	8,2	16,5	2,1	34,6	8,3	3,3	21,0	168,7	31,2	1,7	1,2	**Ca-HCO3**	−3,00
SGW3	9,4	89,4	0,7	1,3	0,1	18,7	10,5	163,5	25,1	1,7[a]	0,2	**Na-HCO3**	−3,50

Comparison of sampled and modelled data – 12th horizon



Comparison of sampled and modelled data – 24th horizon

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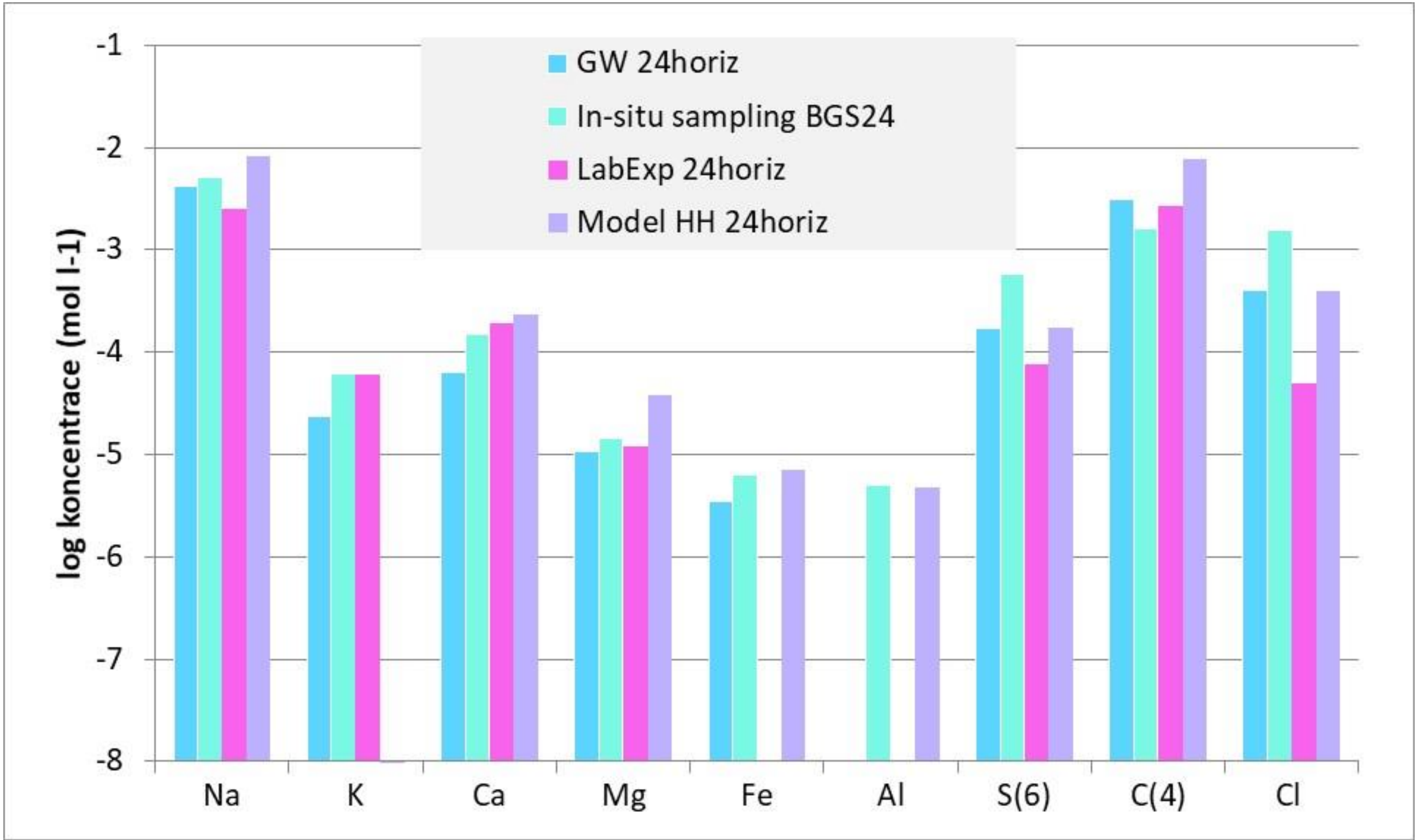

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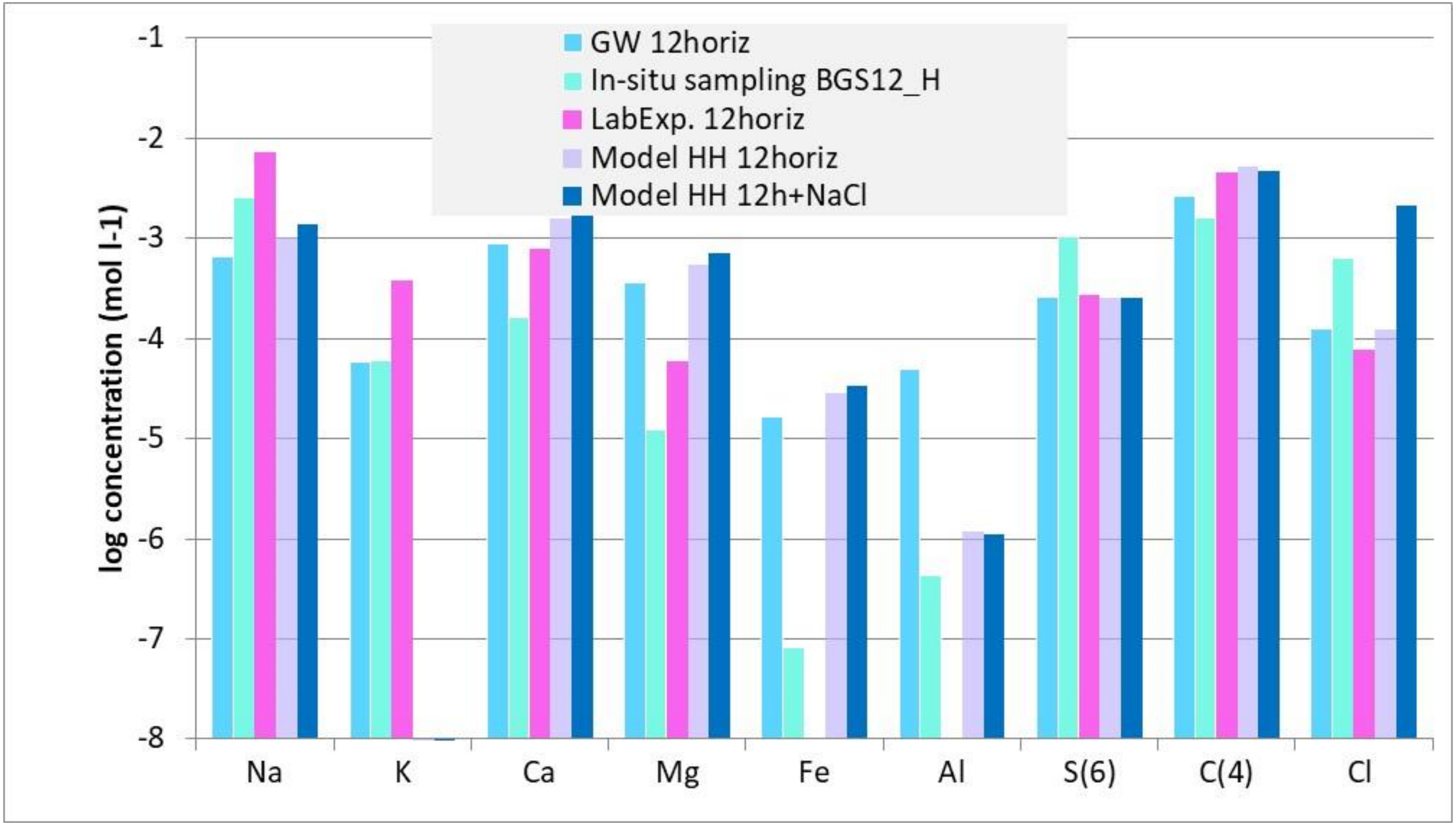
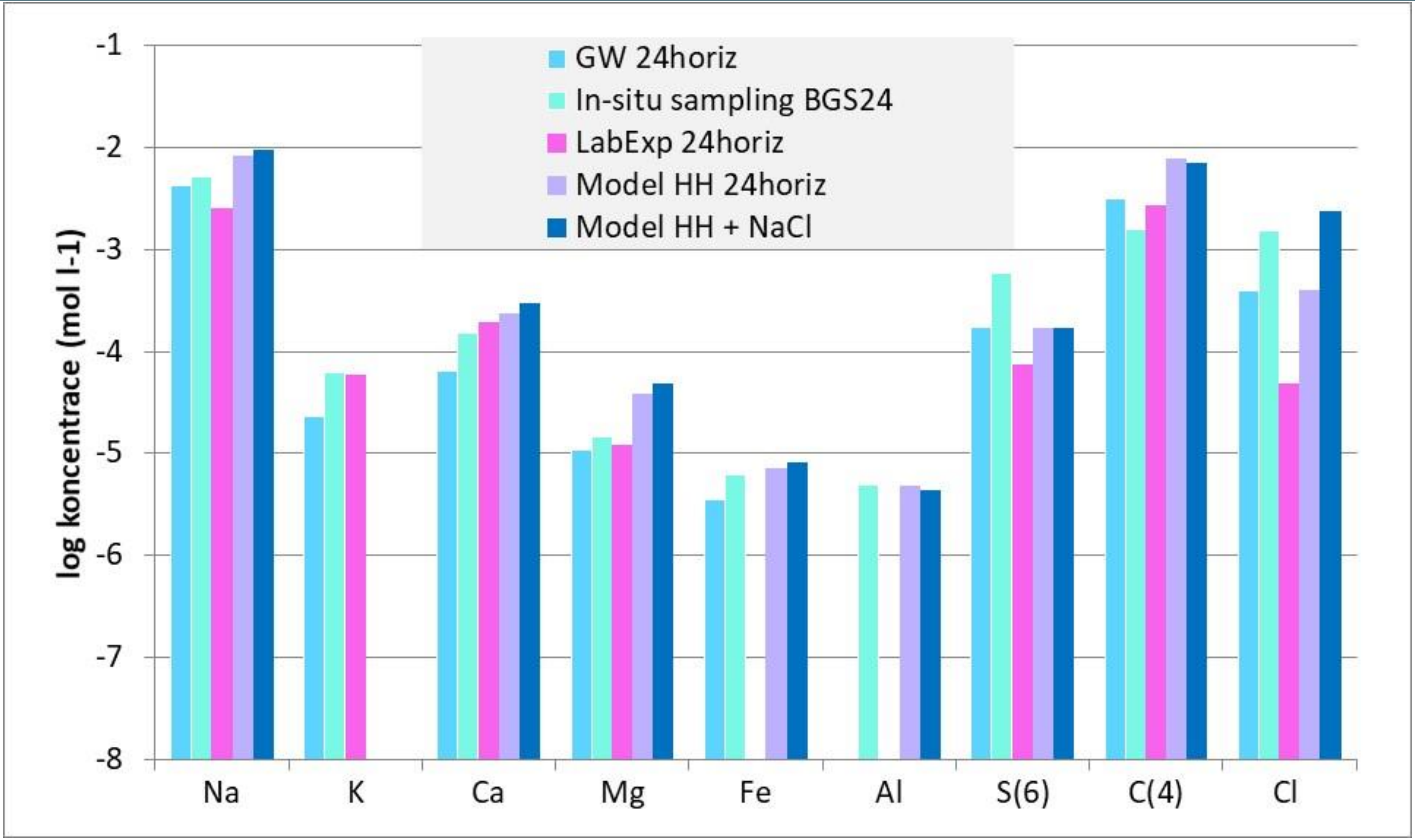
Comparison of sampled and modelled data – 12th horizon; NaCl added



Comparison of sampled and modelled data – 24th horizon; NaCl added



GW zonality at Bukov URF

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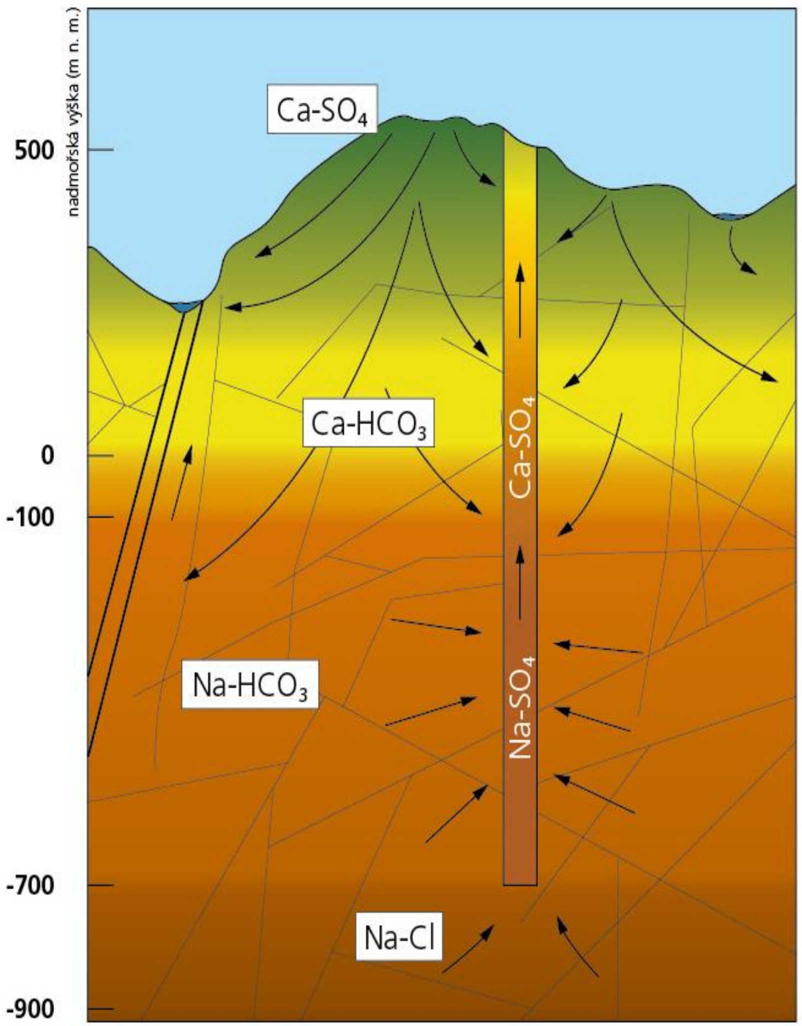

Bukovská a Verner eds. (2017)

- ❑ In case of URF Bukov rock samples, pore water will most probably reflect trend toward Na-Cl-HCO_3 water composition
- ❑ Source of S in in-situ samples: reflects heterogeneity of rock massive and presence of pyrite
- ❑ Source of Cl: fluid inclusions or deep water relicts ??
- ❑ Source of K: still open

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Conclusions

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- None of the techniques, including modelling, is perfect
- Laboratory in-situ out leaching most probably does not fully reflect crystalline rock pore water composition in case of low porosities and heterogeneity of rock massive
- In-situ sampling techniques seems to be more promissing and better reflecting rock heterogeneity; need for longer and more frequent sampling is inevitable

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Acknowledgement

The results has been gained within „Receiving data from deep horizons of Rozna mine“ project, funded by SURAO

Thanks for your attention

Sním

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