EÖTVÖS LORÁND UNIVERSITY FACULTY OF SCIENCES

Origin and formation of carbonate minerals related to natural CO₂ occurrences

by

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I. Introduction and aims

'Carbon capture and storage' (CCS) is widely believed to be capable of attenuating the effect of human CO₂ emissions, while relying on fossil fuels for energy production until alternative sources of energy are developed (IPCC, 2005, 2022). Mineral storage of carbon-dioxide is one of the most promising ways of storing CO₂ safely underground. The study of natural CO₂ reservoirs helps to understand and predict what processes are likely to take place when storing anthropogenic CO₂ underground over geological times (e.g. Baker et al., 1995; Forray et al., 2021; Gao et al., 2009; Gilfillan et al., 2009; Király et al., 2016a; Pearce et al., 1996; Qu et al., 2022). Carbonates in geological systems are very sensitive to the presence and partial pressure of CO₂. Most laboratory experiments (e.g. Cheng et al., 2022; Hellevang et al, 2005) and geochemical models on sandstone reservoirs and CO₂ injection fields predict precipitation of common carbonate minerals (e.g. calcite, dolomite, siderite, magnesite) as well as the formation of a rare carbonate, dawsonite [NaAlCO₃(OH)₂] (e.g., Gaus et al., 2005; Lu et al., 2022; Szabó et al., 2016; Xu et al., 2003, 2005). Dawsonite is believed to be one of the carbon-dioxide "incorporating" minerals in CCS, therefore it is necessary to understand its formation environment, stability, precipitation, and dissolution in the reservoirs over time. Dawsonite mainly crystallizes as a result of high partial pressure of CO₂. To shed light on the precipitation of this carbon-dioxide fixing mineral, and the origin of its formation fluid, three different areas, two from deep saline reservoirs in the Little Hungarian Plain (Ölbő, Mihályi-Répcelak fields, Hungary) and one from a surface occurrence in the Eastern Carpathians (Covasna, Romania) were studied. Stable isotope geochemistry (i.e. $\delta^{13}C$ and $\delta^{18}O$) of carbonate minerals has been widely used to determine the origin of fluids. To be able to measure the stable isotope composition of different carbonates found in sandstones, experimental work was carried out as well in this study. To reveal the precipitation properties and environments of dawsonite (and other cogenetic carbonates), beside detailed petrographical and geochemical investigations, stable isotope analyses were conducted. Additionally to carbon and oxygen isotopes, hydrogen isotope composition of dawsonite was measured for the first time. This might be a new promising tool which can help to constrain the conditions of the dawsonite formation. Finally, to better understand the chemical processes which take place during a CO₂ injection project over 200 years, geochemical modelling was also applied. The well-known and already described sandstones of Mihályi-Répcelak represented the final stage, millions of years after CO₂ flooded the reservoir. Hence,

the dissolution and precipitation of minerals in the modelling results could be validated with the CO₂-flooded sandstones.

II. Study area and samples

Three areas were investigated in this work: 1) Mihályi-Répcelak area is well-known as a natural CO₂ occurrence in the Little Hungarian Plain (Hungary) where the CO₂ trapped (and still produced currently) in a sandstone formation. 2) Ölbő area which is located close to the Mihályi-Répcelak field and where CO₂ is produced from a Miocene limestone reservoir. However, in this study the focus is not on the limestone reservoir, but on the overlying sandstone formation which is identical to those which host the CO₂ in the Mihályi-Répcelak field. The third area is found in Covasna along a creek of Hankó Valley (Eastern Carpathians) and it is famous for the continuous CO₂ emanations (mofettas) and the occurrence of a rare mineral assemblage on the surface.

Mihályi-Répcelak and Ölbő fields

From the Mihályi and Répcelak fields six sandstone reservoirs out of the 26 contain dawsonite (Király et al., 2017), which were selected for this study. From the Ölbő field, 32 core samples were collected from which 7 sandstones and 5 siltstones were selected from the Öl-1, Öl-2, Öl-3 and Öl-6 wells (at 1498-1687.5 m depths) for further investigation. These rocks originate from the same geological formation (Alföldi Formation Group) as the samples from Mihályi and Répcelak fields.

Covasna – Eastern Carpathians

Dawsonite-bearing rock samples were collected in the Hankó Valley, along the creek in Covasna area in 2018 and 2019. Thirteen rock samples were collected from an outcrop and in-situ unconsolidated debris (fluvial deposit) along the creek. Water samples were collected in three different sites in the Hankó Valley, two sampling points were on the bank of the creek where dawsonite was found and one was in a registered spring, located close to the dawsonite sampling sites.

Carbonates for laboratory experiments

Most CCS related studies used isotopic analysis, especially sequential acid extraction (SAE) method to reveal the origin of fluids which drives carbonate formation in a CO₂ reservoir (e.g. Baker et al., 1995; Gao et al., 2009; Liu et al., 2011). The Mihályi-Répcelak and Ölbő sandstones contain various carbonates such as calcite, dawsonite, dolomite, ankerite and

siderite; therefore the applicability of SAE to analyse these kind of samples for stable isotopes are crucial. Liu et al. (2011) reacted whole sandstone samples (containing calcite, dawsonite, ankerite) with 100% orthophosphoric acid at 25 °C for 6 h, 24h and 48 h to extract the CO₂ from carbonates for carbon and oxygen isotope analysis. 6 h reaction time was used for calcite, 24 h dissolution time was applied for dawsonite (based on Baker et al., 1995) and 48 h for ankerite. Cseresznyés (2018) assumed that the orthophosphoric acid starts to dissolve all carbonate minerals at some rate in the sandstone and the isotopic composition of the yielded CO₂ is not representative for a single carbonate. Following on these experiences, new experiments were carried out in this study to achieve more detailed picture, applying different reaction times. First pure carbonate phases (calcite, dolomite, dawsonite, ankerite and siderite) were used to determine their isotopic composition using different reaction times. For the dissolution 1, 6, 12, 24, 36, 48 and 72 hours were applied at 25°C. Dawsonite was synthetized for the lab experiments (used as pure phase and in the artificial mixtures) in order to have pure dawsonite phase which is not contaminated with other minerals and can be used in the experiments. Artificial mixtures (ME1, ME2, ME3) were made by mixing of the pure phases in different ratios. Two natural samples (RM6-9R, RM32-5R2) were selected from the Mihályi-Répcelak field to test the selective acid extraction method. For the dissolution 6, 24 and 48 hours were applied at 25 °C.

III. Methods

Various analytical methods were applied to determine the mineral composition of the rock samples, the water chemistry and the isotopic composition both of the carbonate minerals (pure phases, artificial mixtures and natural samples) and the water samples.

Petrographic features of the natural samples from Mihályi-Répcelak, Olbő and Covasna area were characterized by both optical and electron microscopy. Scanning electron microscopy of the thin sections and fresh broken surface was carried out.

The mineralogical composition of bulk rock powders (<63 μ m), mineral separates and synthetized dawsonite were determined at the Supervisory Authority for Regulatory Affairs (SARA, Budapest, Hungary) with a Bruker D2 Phaser XRD powder diffractometer. Micro X-ray diffraction (MicroXRD) analysis of separated dawsonite and calcite samples were performed at Institute for Geological and Geochemical Research (IGGR, Budapest, Hungary) using a RIGAKU D/MAX RAPID II diffractometer. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was used to identify dawsonite, and to check the presence of dawsonite in the natural samples. Moreover, ATR-FTIR was

applied to check the success of the separation without material loss before the hydrogen isotope measurements. The samples were analysed by a Bruker Vertex 70 Fourier-transformation infrared (FTIR) spectrometer equipped with a Bruker Platinum diamond ATR cell and a DTGS detector at IGGR and SARA. Micro-Raman spectroscopic analysis was used to identify separated dawsonite, siderite, calcite, alumohydrocalcite and to detect minor constituents in the studied samples. The analysis was carried out at the RIRC of the Faculty of Science, ELTE (Budapest, Hungary) with a confocal HORIBA Labram HR800 spectrometer.

Isotope analyses were carried out on the samples used for laboratory experiments (pure phases, artificial mixtures and natural samples) and on the samples from natural CO₂ occurrences (Mihályi-Répcelak, Ölbő and Covasna). H₂O freezing-melting cycles was applied to disintegrate the rock samples, which allows the physical separation of dawsonite and siderite from each other and from other carbonates, to determine their isotopic compositions individually. In case of the Mihályi-Répcelak samples, dawsonite grains were separated by hand picking under stereomicroscope from the 250-63 μ m grain size range. For siderite separation from the Mihályi-Répcelak and Ölbő samples, the same size fractions (250-63 μ m) were used in a Frantz Isodynamic Magnetic Separator at SARA. In case of the Covasna samples, hand-picking was used separate dawsonite.

Stable carbon and oxygen isotope compositions were determined on 150–200 µg of carbonate powders. Carbonate powders were prepared from pure phases, artificial mixtures and natural (bulk) samples. The powders were reacted with orthophosphoric acid at 25 °C for 1, 6, 12, 24, 36 and 72 hours. The same amount of powders were made from the mineral separates, dawsonite and siderite (from Mihályi-Répcelak, Ölbő and Covasna) by reacting the powders with orthophosphoric acid at 72 °C for 1 hour for dawsonite and for 24 hours for siderite (Spötl and Vennemann, 2003; Cseresznyés et al., 2021). The separated CO₂ was analysed, using an automated GASBENCH II sample preparation bench attached to a Thermo Finnigan Delta Plus XP Isotope Ratio Mass Spectrometer (IRMS) at IGGR. Stable hydrogen isotope composition of the hydroxyl group of dawsonite (NaAlCO₃(OH)₂) was determined using an LGR LWIA-24d type laser analyser attached to an in-house built inlet system at IGGR. Stable hydrogen and oxygen isotope analyses of 29 water samples from Covasna were carried out using a Liquid-Water Isotope Analyser-24d manufactured by Los Gatos Research at IGGR (Budapest, Hungary).

Carbonate clumped isotope analysis was carried out on a separated calcite sample from Covasna with a Thermo Scientific 253 Plus 10 kV isotope ratio mass spectrometer (IRMS) at Isotope Climatology and Environmental Research Centre, Atomki (Debrecen, Hungary).

Geochemical modelling was used to simulate the chemical processes which take place after large amount of CO₂ is injected into a sandstone reservoir. For the thermodynamic calculations PHREEQC 3.0 geochemical modelling software (Parkhust and Appelo, 2012) was used with the PHREEQC.dat database. As model inputs the mineral composition of Ölbő sandstones were used. Thermodynamic-batch, kinetic-batch and kinetic-reactive transport models were run with and without supercritical CO₂.

IV. Scientific theses of doctoral study

- 1. The Ölbő and Mihályi-Répcelak areas, as natural laboratories, provided the opportunity to investigate the same sandstone formation which was not flooded naturally by large amount of CO₂ (Ölbő), and compare with a flooded one (Mihályi-Répcelak). The comparison of the petrographic and geochemical features revealed which processes are a response or partially connected to the CO₂ flooding. Dawsonite is missing in the investigated Ölbő sandstone and siltstone samples based on the petrographic investigation and phase analysis (XRD, ATR-FTIR). In Mihályi-Répcelak area dawsonite formation was induced by CO2 flooding in the sandstone reservoir and it can form in the microenvironments in conglomerates as well (Forray et al., 2021). The CO₂-flooding related dissolution process can explain the considerable difference in feldspar and calcite content of sandstones in the two areas. Moreover, the higher abundance of ankerite+siderite associations in Mihályi-Répcelak also suggest that some part of ankerite+siderite could have precipitated during/after the CO₂ inflow. The absence of a second generation of kaolinite in Ölbő field, which probably precipitated after the CO₂ flooding similarly to dawsonite in Mihály-Répcelak area, reinforces the differences between the two studied fields. Geochemical models (PHREEQC) support most of the petrographic observations of the sandstones. According to the kinetic-batch models, the majority of these reactions takes place in the early stages (first 30 years) after CO₂ injection.
- 2. Based on experiments the widely used sequential acid extraction method is not suitable to determine the stable C and O isotopic composition of different carbonate phases from bulk rock. After 6 hours (for calcite), 24 h (for dawsonite) and 48 h (for ankerite) reaction time, the isotopic compositions were not representative for these carbonate minerals. Isotopic

analysis of separated minerals is suggested to gain meaningful data (Cseresznyés et al. 2021). For the preparation of carbonate separates, freezing-melting method is advised because it preserves the shape of the minerals, in contrast to crushing and grinding, which makes easier the hand-picking and the magnetic separation.

- 3. The origin of dawsonite and its parental fluid can be determined by utilizing the carbon isotope composition of dawsonite. The calculated δ^{13} Cco₂ values (-4.8 ‰ -2.0 ‰) in equilibrium with dawsonite in Mihályi-Répcelak overlap with those that are characteristics for mantle/magmatic derived carbon sources and they agree well with the estimation of the European subcontinental lithospheric mantle (SCLM: -3.9 ‰ -2.1 ‰). The isotope values of dawsonite suggest magmatic origin for the majority of the CO₂ from which dawsonite crystallized (Cseresznyés et al., 2021).
- 4. Siderite appears both in the sandstones of Ölbő and Mihályi-Répcelak. It occurs in large patches in both areas, but the Mihályi-Répcelak area shows textures of simultaneous formation with dawsonite. Based on the calculated $\delta^{13}C_{CO2}$ values in equilibrium with siderite in Mihályi-Répcelak, siderites can be discriminated into two groups. In the Group-1 samples, the calculated $\delta^{13}C_{CO2}$ values in equilibrium with siderite (-6.0 \% - -3.9 \%) fall closer to the calculated values from dawsonites and to the European SCLM. This means that, at least one part of the siderite has precipitated as an effect of CO₂ flooding. The inter-mixed of texture dawsonite and siderite in these sandstones also supports this scenario (Cseresznyés et al., 2021). However, in case of Group-2, the calculated $\delta^{13}C_{CO2}$ values (-8.4 % - -6.1 %) are significantly lighter than those calculated from dawsonites and lighter than what was observed in the free CO₂ gas. The calculated $\delta^{13}C_{CO2}$ values (-10.9 ‰ - -6.5 ‰) of siderite from Ölbő overlap with these siderites in Group-2. Thus, the presence of two siderite groups (with distinct isotopic composition) in Mihályi-Répcelak area together with their textural and petrographic features indicate that some part of the siderite could have formed before CO₂ flooding, thus likely represent an early diagenetic mineral, similarly to siderite found in the unflooded Ölbő sandstones.
- 5. Dawsonite provided an exceptional opportunity to determine the origin of pore water during CO₂ flooding as, besides oxygen, it contains hydrogen within its structural OH⁻, and the hydrogen isotope composition of dawsonite has not been determined so far. The results represent the first reported δD values of dawsonite. The estimated stable isotope composition of H₂O present during dawsonite formation in Mihályi-Répcelak

 $(\delta D: -103 \ \% - -74 \ \%, \ \delta^{18}O_{SMOW}: -1.4 \ \% - +4.7 \ \% at 70 \ ^{\circ}C and 98 \ ^{\circ}C, respectively)$ (Cseresznyés et al. 2021) indicate that the parent fluid was meteoric water modified by water-rock interaction.

6. The hydrogeochemical facies of CO2-rich creek and spring water, along the creek of Hankó Valley in Covasna (Romania) is sodium bicarbonate type. According to the stable hydrogen and oxygen isotope analyses, the creek water has meteoric origin (δD : -79.7 ‰ to -56.8 %, $\delta^{18}O_{SMOW}$: -10.9 % to -7.4) meanwhile the spring water shows a mixed origin (δD : -50.9 ‰ to -48.4 ‰, $\delta^{18}O_{SMOW}$: -0.1 ‰ to +2.5 ‰). The higher $\delta^{18}O$ values of the spring water might be related to enhanced water-rock interaction and isotope exchange between CO₂ and H₂O. The detailed petrographic investigation indicates recent surface precipitation of dawsonite in a low-temperature environment (<25°C). The $\delta^{13}C_{CO2}$ values calculated from dawsonite are between -4.1 ‰ and -0.6 ‰, in the same range as the $\delta^{13}C_{CO2}$ values calculated for calcite (-3.3 ‰) found in the dawsonite-bearing rocks. These values agree with the estimated δ^{13} C value of the European SCLM, implying a magmatic CO₂ source. This means that although dawsonite and calcite formed at different temperatures (environments) and times, their parental CO₂ has same magmatic origin. The calculated δD and $\delta^{18}O$ values of dawsonite show similar shift as the spring water, meaning that the formation of dawsonite is related to the spring water and the magmatic CO₂ degassing.

V. Conclusions

Mineral storage of CO₂ is the most promising way to the long-term underground storage of CO₂. Investigation of natural CO₂ occurrences can help to better understand what processes can take place during a CO₂ injection project. Dawsonite is [NaAlCO₃(OH)₂] believed to be a mineral sink of CO₂ which can precipitate as a response of large amount of CO₂ inflow. Three areas (Mihályi-Répcelak, Ölbő; Covasna) were investigated in the Pannonian Basin, which are related to either CO₂ flooding of the rocks or to a continuous CO₂ emanation. The determination of stable isotope composition of carbonates is a widely used way to reveal the origin of their source fluid. Unfortunately, the separation of carbonates from rocks containing a complex carbonate assemblage is not possible with the widely used sequential acid extraction method. However, mineral separates proved to be an excellent tool to gain reliable isotopic results for the different carbonates.

Dawsonite and siderite were separated from the sandstones of Mihályi-Répcelak and Ölbő fields for C and O isotope analyses. The CO₂ that precipitated as dawsonite seems to be magmatic in origin having also similar isotopic composition to that of European Subcontinental Lithospheric Mantle. In contrast, the isotopic signature of siderite suggests that it was partially formed as a response to CO₂ flooding, the rest being an early diagenetic mineral. The isotopic composition of siderite present in the unflooded Ölbő sandstones also supports this scenario. To better understand the processes in these sandstones, geochemical models were created. The Ölbő and Mihályi-Répcelak areas, as natural laboratories, provided an opportunity to validate these geochemical models, both before interaction with CO₂ (Ölbő samples) and after millions of years being in contact with CO₂ (Mihályi-Répcelak samples). The models shown that most observed reactions can happen just 30 years after CO₂ injection.

In the Covasna area dawsonite formation is observed in surface environment. Mineral separates (dawsonite, calcite) and surface water samples were used to determine their isotopic composition. The creek water has meteoric origin, meanwhile the spring water shows a mixed origin. Occurrence of dawsonite indicates recent surface precipitation, in a low-temperature process ($<25^{\circ}$ C). Dawsonite precipitation is probably related to the continuous CO₂ degassing which originates from the magma. Calcite and dawsonite precipitated from the same CO₂ source, but in different processes and time. Dawsonite precipitated from the spring water and the continuous CO₂ outflow, which caused a positive shift in the oxygen isotope composition of the spring water.

VI. References

- Baker, J.C., Bai, G.P., Hamilton, P.J., Golding, S.D., Keene, J.B., 1995. Continental-Scale Magmatic Carbon Dioxide Seepage Recorded by Dawsonite in the Bowen-Gunnedah-Sydney Basin System, Eastern Australia. J. Sediment. Res. 65, 522–530. <u>https://doi.org/10.1306/d4268117-2b26-11d7-8648000102c1865d</u>
- Cheng, J., Yu, H., Liu, N., Yu, Y., Ahmat, K., Zhao, R., 2022. Experimental investigation for the impact of chlorite dissolution on CO₂ mineral trapping in a sandstone-brine-CO₂ system. Greenh. Gases Sci. Technol. 12, 470–485. https://doi.org/10.1002/ghg.2163
- Cseresznyés, D. 2018. Szén-dioxid felszín alatti tárolásához kapcsolódó karbonátok stabil izotóp összetételének meghatározása. MSc dolgozat, Eötvös Loránd Tudományegyetem, Budapest, pp. 50.
- Cseresznyés, D., Czuppon, G., Király, C., Demény, A., Györe, D., Forray, V., Kovács, I., Szabó, C., Falus, G., 2021. Origin of dawsonite-forming fluids in the Mihályi-Répcelak field (Pannonian Basin) using stable H, C and O isotope compositions: Implication for mineral storage of carbon-dioxide. Chem. Geol. 584. https://doi.org/10.1016/j.chemgeo.2021.120536
- Forray, V., Király, C., Demény, A., Cseresznyés, D., Szabó, C., Falus, G., 2021. Mineralogical and geochemical changes in conglomerate reservoir rocks induced by CO₂ influx at Mihályi-Répcelak natural analogue, NW-Hungary. Environ. Earth Sci. 80, 1–12. https://doi.org/10.1007/s12665-021-10050-9
- Gao, Y., Liu, L., Hu, W., 2009. Petrology and isotopic geochemistry of dawsonite-bearing sandstones in Hailaer basin, northeastern China. Appl. Geochemistry 24, 1724–1738. https://doi.org/10.1016/j.apgeochem.2009.05.002
- Gaus, I., Azaroual, M., Czernichowski-Lauriol, I., 2005. Reactive transport modelling of the impact of CO₂ injection on the clayey cap rock at Sleipner (North Sea). Chem. Geol. 217, 319–337.

https://doi.org/10.1016/j.chemgeo.2004.12.016

- Gilfillan, S.M.V., Sherwood Lollar, B., Holland, G., Blagburn, D., Stevens, S., Schoell, M., Cassidy, M., Ding, Z., Zhou, Z., Lacrampe-Couloume, G. and Ballentine, C.J. 2009. Solubility trapping in formation water as dominant CO₂ sink in natural gas fields. Nature 458, 614-618, 10.1038/nature07852.
- Hellevang, H., Aagaard, P., Oelkers, E.H., Kvamme, B., 2005. Can dawsonite permanently trap CO2? Environ. Sci. Technol. 39, 8281–8287. https://doi.org/10.1021/es0504791
- IPCC 2005. IPCC special report on carbon dioxide capture and storage. Metz, B., Davidson, O., de Coninck, H.C., Loos, M., Meyer, L.A. (Eds.), Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom/New York, NY, USA.
- IPCC, 2022.Climate Change 2022 Impacts, Adaptation, and Vulnerability. Contribution of Working Group II to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [H.-O. Pörtner, D.C. Roberts, M. Tignor, E.S. Poloczanska, K. Mintenbeck, A. Alegría, M. Craig, S. Langsdorf, S. Löschke, V. Möller, A. Okem, B. Rama (eds.)]. Cambridge University Press. Cambridge University Press, Cambridge, UK and New York, NY, USA, 3056 pp., doi:10.1017/9781009325844.
- Király, C., Sendula, E., Szamosfalvi, Á., Káldos, R., Kónya, P., Kovács, I.J., Füri, J., Bendő, Z., Falus, G., 2016a. The relevance of dawsonite precipitation in CO₂ sequestration in the Mihályi-Répcelak area, NW Hungary. Geol. Soc. London, Spec. Publ. 435, 405–418. https://doi.org/10.1144/sp435.15
- Király, C., Szabó, Z., Szamosfalvi, Á., Kónya, P., Szabó, C., Falus, G., 2017. How much CO2 is trapped in carbonate minerals of a natural CO₂ occurrence? Energy Procedia 125, 527–534. https://doi.org/10.1016/j.egypro.2017.08.180
- Lu, P., Zhang, G., Huang, Y., Apps, J., Zhu, C., 2022. Dawsonite as a Temporary but Effective Sink for Geological Carbon Storage. Int. J. Greenh. Gas Control 119, 103733. https://doi.org/10.1016/j.ijggc.2022.103733
- Parkhurst, D.L., Apelllo, C.A.J. 2013. Description input and examples for PHREEQC version 3 A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497.
- Pearce, J., Holloway, S., Wacker, H., Nelis, M., Rochelle, C., Bateman, K., 1996. Natural occurrences as analogues for the geological disposal of carbon dioxide. Energy Convers. Manag. 37, 1123–1128.
- Spötl, C., Vennemann, T.W., 2003. Continuous-flow isotope ratio mass spectrometric analysis of carbonate minerals. Rapid Commun. Mass Spectrom. 17, 1004–1006. https://doi.org/10.1002/rcm.1010
- Szabó, Z., Hellevang, H., Király, C., Sendula, E., Kónya, P., Falus, G., Török, S., Szabó, C., 2016. Experimental-modelling geochemical study of potential CCS caprocks in brine and CO₂-saturated brine. Int. J. Greenh. Gas Control 44, 262–275. https://doi.org/10.1016/j.ijggc.2015.11.027
- Xu, T., Apps, J.A., Pruess, K., 2003. Reactive geochemical transport simulation to study mineral trapping for CO₂ disposal in deep arenaceous formations. J. Geophys. Res. Solid Earth 108, 2071. https://doi.org/10.1029/2002jb001979
- Xu, T., Apps, J.A., Pruess, K., 2005. Mineral sequestration of carbon dioxide in a sandstone-shale system. Chem. Geol. 217, 295–318. https://doi.org/10.1016/j.chemgeo.2004.12.015

VII. Publications related to doctoral study

1.1. Papers published in peer-reviewed scientific journals

- Cseresznyés, D., Czuppon, G., Király, C., Demény, A., Györe, D., Forray, V., Kovács, I., Szabó, C., Falus, G., 2021. Origin of dawsonite-forming fluids in the Mihályi-Répcelak field (Pannonian Basin) using stable H, C and O isotope compositions: Implication for mineral storage of carbon-dioxide. Chem. Geol. 584. https://doi.org/10.1016/j.chemgeo.2021.120536
- Forray, V., Király, C., Demény, A., Cseresznyés, D., Szabó, C., Falus, G., 2021. Mineralogical and geochemical changes in conglomerate reservoir rocks induced by CO₂ influx at Mihályi-Répcelak natural analogue, NW-Hungary. Environ. Earth Sci. 80, 1–12. <u>https://doi.org/10.1007/s12665-021-10050-9</u>
- 1.2. Selected conference abstracts

- Cseresznyés, D., Király, Cs., Szabó-Krausz, Zs., Szamosfalvi, Á., Szabó, Cs., Falus, Gy. & Czuppon, Gy. (2022) Observed and modeled geochemical interactions in a CO₂-porewater-sandstone system. AAPG Europe Regional Conference 2022, 3-4 May 2022, Budapest (Hungary), Book of Abstracts, 74.
- Cseresznyés, D., Király, Cs., Szabó-Krausz, Zs., Szamosfalvi, Á., Szabó, Cs., Falus, Gy. & Czuppon, Gy. (2021) Petrographic and geochemical investigation of naturally CO₂-free and CO₂-flooded sandstones from the Central Pannonian Basin. European Geosciences Union General Assembly 2021, April 19-30, Virtual Meeting, EGU2021-16131
- Cseresznyés, D., Király, Cs., Szabó-Krausz, Zs., Szamosfalvi, Á., Szabó, Cs., Falus, Gy. & Czuppon, Gy. (2021) Interactions in CO2-porewater-sandstone system, International Symposium on Geofluids, 7-9 July 2021, Virtual Meeting, Book of Abstracts, 59.
- 4. Cseresznyés, D., Király, Cs., Szabó-Krausz, Zs., Szamosfalvi, Á., Szabó, Cs., Falus, Gy. & Czuppon, Gy. (2021) Interactions in Pannonian sandstones as an effect of CO₂ inflow (*in Hungarian*), 11th Assembly of Petrology and Geochemistry, 2-4 September 2021, Sopron (Hungary), Book of Abstracts, 16.
- Cseresznyés, D., Király, Cs., Szabó-Krausz, Zs., Szamosfalvi, Á., Szabó, Cs., Falus, Gy. & Czuppon, Gy. (2021) Petrographic and isotopic characteristics of carbonates from naturally CO₂-free and CO₂flooded sandstones. 18th Stable Isotope Network Austria Meeting, 11-12 November 2021, Tulln (Austria), Book of Abstracts, 25.
- Cseresznyés, D., Czuppon, Gy., Király, Cs., Györe, D., Gilfillan, S., Kesjár, D., Demény, A., Szabó, Cs. & Falus, Gy. (2020) Stable isotope composition of dawsonite from different environments: implication for constrain the origin and formation condition. 30th Goldschmidt Conference, June 21-26., Virtual Meeting
- Cseresznyés, D., Király, Cs., Király, E., Czuppon, Gy., Magyar, N., Szabó, Cs. & Falus Gy. (2019) Effect of CO₂ on the geochemical properties of carbonates. 29th Goldschmidt Conference, August 18-23, Barcelona (Spain), Goldschmidt 2019 Conference Abstracts, unpaged.
- 8. **Cseresznyés, D.**, Király, Cs., Czuppon, Gy., Demény, A., Szabó, Cs., & Falus, Gy. (2019) Stable isotope study of a natural CO₂ occurrence in the Pannonian Basin. SAGES Global Climate Challanges for a Blue Green Economy, November 27-28., Edinburgh (United Kingdom)
- Cseresznyés, D., Czuppon, Gy., Király, Cs., Papucs, A., Szabó, Cs., Demény, A. & Falus Gy. (2019) Dawsonite from surface environment, Covasna (Romania): preliminary results. 17th Stable Isotope Network Austria, November 8-9., Absam, (Austria)
- Cseresznyés, D., Király, Cs., Czuppon, Gy., Szabó, Cs. & Falus, Gy. (2019) Natural CO₂ occurrence in the Pannonian Basin: determination of geochemical parameters and stable isotope composition of CO₂bearing sandstones and their implications to the fluid system. International Lithosphere Program, October 15-19., Hévíz (Hungary)
- Cseresznyés, D., Czuppon, Gy., Király, Cs., Papucs, A., Kovács, I., Szabó, Cs. & Falus Gy. (2019) Determination of dawsonite stable isotope composition from Kovászna, 15th Environmental Science Conference of the Carpathian Basin, April 03-06, 2019, Kolozsvár (Transylvania), Book of Abstracts, 74-75.
- 12. **Cseresznyés**, **D.**, Czuppon, Gy., Király, Cs., Szabó, Zs, Szabó, Cs., Demény, A., Dietzel, M., Purgstaller, B., Vasileios, M. & Falus, Gy. (2018) Stable isotope compositions of dawsonite and other carbonates from the West-Hungarian natural CO₂ occurrence: implication for their origin. Stable Isotope Network Austria, November 22-23, 2018, Graz (Austria), 24.
- Cseresznyés, D., Czuppon, Gy., Király, Cs., Papucs, A., Kovács, I., Falus, Gy. & Szabó, Cs. (2018) Stable C, O and H isotope composition of dawsonite from Covasna: implications for the origin of CO₂. XX. Geologist Meeting in Szeklerland, October 25-28, 2018, Sepsiszentgyörgy (Transylvania), 30.
- Cseresznyés, D., Czuppon, Gy., Király, Cs., Forray, V., Papucs, A., Kovács, I., Falus, Gy. & Szabó, Cs. (2018) Stable isotope composition of dawsonite in surface environment. 9th Assembly of Petrology and Geochemistry, September 6-8, 2018. Szentkút (Hungary), 47-48.
- 1.3 Further publications
 - Király, C., Cseresznyés, D., Magyar, N., Hatvani, I.G., Egedy, T., Szabó-Krausz., Zs., Udvardi, B., Jakab, G., Varga, G., Szalai, Z., 2023. The role of water and weathering processes in landslides in Hungarian loess sediments. Hydrology, 10, 4, 81. <u>https://doi.org/10.3390/hydrology10040081</u>
 - Cseresznyés, D., Czuppon, Gy., Szabó, Zs., Király, Cs., Szabó, Cs., 2017. Stable isotope compositions of different mineral phases found in a natural CO₂-reservoir (NW-Hungary): implication for their origin. Energy Procedia, 114, 2812-2818. <u>10.1016/j.egypro.2017.03.1399</u>