

# Caprock analysis from the Mihályi-Répcelak natural CO<sub>2</sub> occurrence, Western Hungary

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**Abstract** Caprock integrity is one of the most important factors regarding the long-term safe underground storage of CO<sub>2</sub>. As a result of geochemical reactions among the caprock mineralogy and CO<sub>2</sub> saturated pore water, the physical properties of caprock such as porosity, permeability may change, which could affect its sealing capacity. Natural CO<sub>2</sub> occurrences can help to understand these long term reactions under storage conditions on geological timescale. Our study area, the Mihályi-Répcelak natural CO<sub>2</sub> occurrence, is believed to be leak-proof system on geological timescale. To identify and understand the mineral reactions in the caprocks we applied XRD, FTIR-ATR and SEM analysis of drill cores derived from the study area. The petrophysical properties of the studied rock samples were determined from the interpretation of geophysical well-logs and grain size distribution. The effective porosity (~4 %), permeability (0.026 mD) and clay content (~80 %) of the drill cores imply that the studied clayey caprocks represent an adequate physical barrier to the CO<sub>2</sub>. Our analytical results show that dawsonite has formed within the caprocks. In most cases the dawsonite crystallized after albite dissolution. This implies that CO<sub>2</sub> or CO<sub>2</sub>-saturated brine can penetrate into the caprock resulting in mineral reactions and most likely changing the porosity and permeability of the sealing lithology. On the other hand the caprock may react as a geochemical buffer for the CO<sub>2</sub> and, at least part of it, can be stored within the

caprock as solid phase, thereby increasing the storage capacity of the system.

**Keywords** Natural CO<sub>2</sub> occurrence · Caprock analysis · Physical properties · Dawsonite · Pannonian Basin

## Introduction

The significance of caprocks in carbon dioxide geological storage activities is to prevent the escape of CO<sub>2</sub> to other reservoirs or to the surface even over geological time scales. This sealing nature of the caprocks is the consequence of their low permeability and porosity, high sorption and cation exchange capacity, especially in case of clayey lithologies. In addition to these parameters, it is also essential to understand the geochemical properties of the caprocks and their long term response to the presence of CO<sub>2</sub> (Stevens et al. 2006; Kaldi et al. 2011; Liu et al. 2012; Kaldi et al. 2013). The migration ‘pathway’ of CO<sub>2</sub> through the caprock can lead through fractures. Molecular diffusion may also be an important mode of migration through the caprock lithologies. As an effect of CO<sub>2</sub>—water—caprock interaction the physical and geochemical properties of the caprock can alter, which may lead to decreasing effectiveness of the sealing properties of the caprock and could potentially result in unwanted leakage (Gaus 2010; Kaldi et al. 2011). On the other hand, the reacting caprock may serve as an additional sink for the injected CO<sub>2</sub> thereby increasing the amount of carbon dioxide that can be stored in mineral phase.

A number of studies have been made on how CO<sub>2</sub> injection influences the mechanical behaviour of caprocks (e.g., Shukla et al. 2010). Many of the experiments demonstrated that injected CO<sub>2</sub> could influence pore

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geometry and thereby the sealing performance of clayey caprocks (e.g., Gaus 2010; Heath et al. 2011; Navarre-Stichler et al. 2011). According to Liu et al. (2012), at least part of these changes may be related to mineral reactions taking place between the CO<sub>2</sub>—brine—caprock system. Studies focusing on the potential geochemical reactions in the caprocks (i.e., Credoz et al. 2009; Kohler et al. 2009; Alemu et al. 2011; Liu et al. 2012) showed that mobilization, dissolution and re-precipitation of carbonates is very likely. Changes in clay mineralogy and mineral chemistry is also suggested, however the precise quantification of this phenomenon with X-ray is difficult due to small quantities of reactants (Liu et al. 2012).

In the process of understanding caprock behaviour in the presence of natural CO<sub>2</sub> occurrences can help to recognize which properties of caprock lithologies are the most important contributors that provide closure even on geological time scales. Knowledge of the long term effect of CO<sub>2</sub> on the caprock is fundamental in selecting a potential CO<sub>2</sub> injection site. During normal commercial operations the reservoir is typically core sampled, but the caprock is not (Stevens et al. 2006).

In this paper we provide mineralogical and geochemical data on caprock lithology of a natural CO<sub>2</sub> reservoir at Mihályi-Répcelak area (Western Hungary) (Fig. 1), where the buoyant migration of CO<sub>2</sub> does not reach the surface or shallow subsurface (Mészáros et al. 1979; Pearce et al. 2005). This study may contribute to our knowledge about potential mineral reactions, which can occur in caprocks.

Exploration of the study area was started in 1933 with geophysical measurements. The industrial production of CO<sub>2</sub> started in the 1940s from the three largest reservoirs (Mészáros et al. 1979). This field is an excellent study area for the potential CO<sub>2</sub> injection sites in the Pannonian Basin, where industrial CO<sub>2</sub> could be stored in reservoirs with the

same lithological facies (e.g. in Hungary and its neighbouring countries) as the Mihályi-Répcelak natural occurrence (Király et al. 2016).

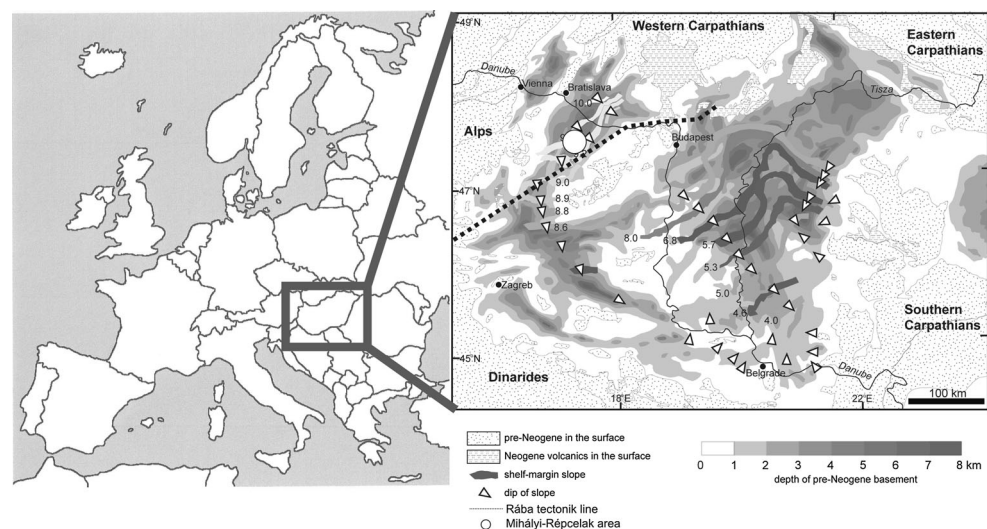
In order to determine the petrophysical and mineralogical properties of the studied natural CO<sub>2</sub> occurrence, we applied the following analysis. The samples, coming from drill cores, were measured by X-ray diffractometer (XRD), Fourier-transform infrared spectrometer (FTIR), scanning electron microscope (SEM) to record modal compositions and specific mineral properties within the studied caprock samples. Furthermore, the petrophysical properties are estimated using well-logs and grain size distribution analysis.

## Geological background

Intensive sedimentation characterized the Pannonian Basin in Late Miocene (10–9 Ma). The sediments were deposited by fluvial systems from the NW to the SE direction. The sequence includes sediments from deep basin to the delta plane facies. In the sedimentary succession turbiditic sandstones and clayey layers alternate (Juhász 1991; Magyar et al. 2013). In the Pannonian Basin these sediments are widespread (Fig. 1), containing oil, natural gas and CO<sub>2</sub>. Mihályi-Répcelak area (W-Hungary) is one of the largest natural CO<sub>2</sub> occurrences in the Pannonian Basin (Mészáros et al. 1979) (Fig. 1).

According to the most recent studies on the source of CO<sub>2</sub> (Palcsu et al. 2014; Vető et al. 2014), the sandstone reservoirs were firstly filled with oil generated 8–7 Ma. It is assumed that CO<sub>2</sub> was liberated from an early Pliocene (7–4 Ma) mafic intrusion and migrated upward along the Rába tectonic line (Fig. 1), finally, replaced the oil in the siliciclastic reservoirs (approximately 4 Ma) (Palcsu et al.

**Fig. 1** Map of Europe and the Pannonian Basin, showing the progress of filling of the Pannonian Basin, *white point* indicates the Mihályi-Répcelak study area (modified after Magyar et al. 2013)



2014; Vető et al. 2014). Recently, 26 CO<sub>2</sub> fields and 2 mixed-gas fields are known in the Mihályi-Répcelak area in the Pannonian sediments and the basement rocks (Mészáros et al. 1979). The original CO<sub>2</sub> gas in place is approximately 25 million tons, from which about 100,000 tons are produced annually since the '40 s (Mészáros et al. 1979).

## Characterization of the sealing lithologies

In the following section we provide a comprehensive overview on the properties of sealing clayey lithologies that separate the sandstone CO<sub>2</sub> reservoirs.

### Calculation of clay content, effective porosity and permeability in the sealing layers

We used corrected and inter-correlated basic well-logs (SP, resistivity log for the geophysical interpretation), because the porosity logs were missing from most of the area (Szamosfalvi 2014). The re-processing and re-interpretation of well-logs was carried out by the WellCAD software. To estimate the electric sand content (eh), we used the following formula (Zilahi-Sebess 2009):

$$eh = \frac{\log(R) - av}{hv - av} \quad (1)$$

where, av = clay base line, hv = sand base line, R = resistivity (ohmm).

From these data we calculated the clay content (esh) with the following equation (Zilahi-Sebess 2009):

$$esh = \frac{1 - eh + |1 - eh|}{2} \quad (2)$$

In order to define the clay and sand baselines and estimate the clay content, measured resistivity logs were used. In this case we fitted the clay and sand baselines on the full length of the resistivity logs. This method eliminated the change in resistivity related to temperature (Szamosfalvi 2014).

In case of the trend effective porosity estimation a compaction trend, resulting from recent depth and from the implied diagenetic history, has been considered. The equation is based on the method of Mészáros (2001) which has been modified as follows.

$$tep = (0.11 \times e^{-1 \times (0.0008 \times DEPTH)^4} + 0.26 \times e^{-1 \times (0.00051 \times DEPTH)^4}) \times eh \quad (3)$$

where, tep = trend effective porosity

DEPTH = depth (m)

eh = electric sand content (–)

Trend effective porosity is the expected effective porosity according to the compaction versus depth, it is the product of the expected total porosity as a function of depth and the sand content. The permeability estimation is based on the resistivity logs. We calculated the results with the modified Timur equation (Zilahi-Sebess 2008). First time we estimated the filtration coefficient (K),

$$K(m/s) = \frac{0.136 \times 10^{-5} \times tep^{4.4}}{((1 - eh) \times 0.14)^2} \quad (4)$$

then we converted the results to permeability, the results are in the Table 1. The filtration coefficient equivalent to 1 D permeability is approximately 10<sup>–5</sup> m/s (Zilahi-Sebess 2008).

### Grain size distribution

Grain size distribution measurements were performed with Horiba LA-950V2 (Eötvös University, Budapest). A freezing/melting procedure was carried out on most of the samples to disintegrate cemented rocks. This disintegration was assisted by ultrasound bath in Na-pyrophosphate-water mixture.

### Scanning electron microscopy (SEM)

The rock samples were analysed by SEM at Eötvös University. The instrument is an AMRAY 1830 I/T6 equipped with EDAX PV 9800 energy dispersive X-ray spectrometer. During the analyses the accelerating voltage was 20 kV and the primary sample current was 1–2 nA. Thin sections and artificially fractured surfaces were studied. Back-scattered electron images (BSE) and secondary electron images (SE) were taken from the polished surface and artificially fractured surfaces, respectively. With this method the texture, type and composition of minerals and diagenetic processes were observed.

### X-ray powder diffraction (XRD)

All samples (Table 1) were analysed by XRD at Geological and Geophysical Institute of Hungary (MFGI). For the X-ray powder diffraction analysis a Phillips PW 1730 diffractometer (Cu cathode, 40 kV and 30 mA tube-current, graphite monochromator, goniometer speed 2°/min) and powdered samples of whole rocks (<63 μm) were used. A semi-quantitative assessment of the relative concentrations of phases was performed by relative intensity ratios and half width of specific reflections of minerals by using XDB Powder Diffraction Phase Analytical software 2.7.

**Table 1** Calculated physical conditions and CO<sub>2</sub> concentrations in the studied caprocks from Mihályi-Répcelak area and related CO<sub>2</sub> reservoirs, respectively (NAD: no available data)

Sample	Depth (m)	Temperature <sup>a</sup> (°C)	CO <sub>2</sub> in the related reservoir (%)	Clay content <sup>a</sup>	Permeability (mD)	Trend effective porosity
RM6-2B	1280–1287	62.48	95.7	0.75	0.062	0.06
RM19-6C	1394–1411.5	67.46	97.6	0.85	0.019	0.03
RM19-6B	1394–1411.5	67.46	97.6	0.85	0.019	0.03
RM6-6C	1399.5–1417	67.68	97.4	0.73	0.047	0.06
RM6-7C	1417–1425.4	68.02	97.9	0.73	0.051	0.06
RM6-8BC	1425.4–1443.5	68.74	NAD	0.79	0.013	0.04
RM6-9C	1443.5–1461	69.44	NAD	0.84	0.004	0.04
RM46-4/1C	1461–1478	70.12	95.4	0.70	0.066	0.06
RM46-4/2C	1461–1478	70.12	95.4	0.70	0.066	0.06
RM46-6B	1495–1512	71.48	NAD	0.78	0.012	0.04
RM46-7/1C	1626.5–1643.5	76.74	92.8	0.82	0.002	0.03
RM46-7/2C	1626.5–1643.5	76.74	92.8	0.82	0.002	0.03
RM46-7/2B	1626.5–1643.5	76.74	92.8	0.84	0.001	0.03

<sup>a</sup> Based on the interpretation of geophysical well-logs

### Infrared spectrometry (ATR-FTIR)

All samples were analysed by a Fourier–transform infrared spectrometer (Bruker Vertex 70) with a single pass ATR cell (Bruker Platinum diamond ATR) and an MCT detector was used to obtain ATR spectra in the mid-infrared spectral range (400–4000 cm<sup>−1</sup>) at MFGI. The samples were powdered and were dried for 30 min at 80 °C in an oven immediately prior to the ATR FTIR measurements. This process provided that the majority of the adsorbed water was removed (Udvardi et al. 2014). The relatively low temperature of the heat treatment guarantees that it does not cause any first order alterations in the clay mineral structures but facilitates significantly the interpretation of the ATR spectra (Tóth et al. 2012). This method is pronouncedly sensitive to the presence of OH<sup>−</sup>-bearing minerals. By means of the second derivate, the location and interval of main absorption bands can be verified.

### Characterization of the sediments

#### Physical properties of samples

The analysed samples were collected from caprocks of the natural CO<sub>2</sub> reservoirs. The original and estimated physical conditions of caprocks are shown in Table 1. The pressure is hydrostatical in this system (Mészáros et al. 1979), the temperature was calculated from geothermal gradient (40 °C/km) (Dövényi et al. 1983) and average surface temperature (11 °C). The supercritical CO<sub>2</sub> concentration

of the gas phase in the related reservoirs is >90 %. Other gases in the reservoirs are N<sub>2</sub> (4 %), CH<sub>4</sub> (5 %), HC's (1 %). The water—CO<sub>2</sub> ratio in the reservoirs is approximately 35–65 (Mészáros et al. 1979). Amount of CO<sub>2</sub> decreases towards the surface and CO<sub>2</sub> cannot be detected above 1100 m (Mészáros et al. 1979). The results of well-log analysis (i.e., clay content, trend effective porosity and permeability) are given in Table 1. The data show that the average clay content is 79 %, the average trend effective porosity is 4 % and the average permeability is 0.026 mD in the studied caprocks.

#### Grain size distribution

The results of grain size distribution analysis are shown in Table 2. Four studied samples (RM19-6C, RM6-6C, RM46-4/1C, RM46-7/1C) were not measured because these siltstones did not disintegrate despite the physical treatment (ultrasound, freezing-melting). The results show that the studied rocks can be divided in three groups according to the grain size distribution. Sample RM19-6B has a single peak (12.4 μm). Four samples (RM46-6B, RM6-2B, RM6-7C, RM6-9C) have one peak (13.5 ± 0.9 μm) and a 'shoulder' (53.5 ± 3.3 μm). The rest of the samples (RM46-4/2C, RM46-7/2C, RM6-8BC) have two peaks (13 ± 1 μm and 60.5 ± 5 μm), sample RM46-7/2B is different because the first peak is at colloidal grain size (0.32 μm) and the other peak is at 9.39 μm. The average grain size of all samples studied is 33.25 ± 10.5 μm (Table 2). Furthermore, the grain size distribution analysis shows that the average clay fraction is

**Table 2** Results of grain size distribution analyses of the studied caprocks

Sample	Average ( $\mu\text{m}$ )	1. peak ( $\mu\text{m}$ )	2. peak ( $\mu\text{m}$ )	Comment of 2nd peak	Clay fraction* (%)	Silt fraction (%)
RM19-6B	21.2	12.4			7.6	87.4
RM46-4/2C	45.7	14.1	63.1		3.1	74
RM46-6B	31.1	13.3	54.7	Only shoulder	2.5	85.8
RM46-7/2B	12.3	0.3	9.4		17.8	81.3
RM46-7/2C	40.5	12.3	54.7		3.4	77.9
RM6-2B	38.8	14.1	55.5	Only shoulder	3.0	79.5
RM6-7C	34.1	14.3	48.5	Only shoulder	8.4	75.6
RM6-8BC	40.0	12.5	63.6		4.7	75.6
RM6-9C	35.7	12.3	55.1	Only shoulder	3.1	82

Note that Clay fraction is determined based only on grain size ( $<4.47 \mu\text{m}$ ), it has no direct relation with mineralogy. Note strong relation between Silt fraction ( $67.53\text{--}4.47 \mu\text{m}$ ) and Clay content in Table 1

$5.8 \pm 5.2 \%$  and the average silt fraction is  $79.9 \pm 5 \%$  (Table 2).

### Petrography

The samples are from coarse to fine grained siltstones (Table 2). The caprocks are grey and/or brown in colour. Carbonate cement (calcite, ankerite and siderite) and organic material are found in all (Fig. 2a, b). Fractures were observed neither on macroscopic nor on microscopic scale. The data of SEM (secondary electron images and back-scattered electron images) analyses were used to discriminate detrital and diagenetic minerals. Detrital minerals in the samples are quartz, feldspar (plagioclase, K-feldspar), mica and dolomite. The micas are mainly oriented, parallel to the lamination, ankerite or siderite rim can be found on dolomite. Feldspars (plagioclase, K-feldspar) indicate dissolution features (Fig. 2a, c). The secondary electron images show that diagenetic minerals are carbonate minerals (calcite, ankerite, siderite) mostly in the cement (Fig. 2b), further diagenetic minerals are clay minerals (illite, kaolinite) and dawsonite. The diagenetic dawsonite crystals occur only in the close vicinity of partially or completely dissolved feldspars (Fig. 2a, c, d).

### Mineral composition

The XRD results show that the mineral composition of the caprocks (quartz (29.2 m/m %), dolomite+ankerite (20.3 m/m %), muscovite (15.3 m/m %), calcite (9.4 m/m %), kaolinite (8.5 m/m %), illite (8 m/m %), siderite (3.3 m/m %), K-feldspar (1.5 m/m %), plagioclase (1.9 m/m %)) is highly similar to that of the reservoirs (Király et al. 2016). However, the volume ratio of the constituent minerals is different (Table 3) in the caprock and the reservoir lithology. The main difference between the reservoir and the caprock is in the quantity of illite (reservoir: 1.8 m/m %; caprock: 8 m/

m %), quartz (reservoir: 46.6 m/m %; caprock: 29.2 m/m %), calcite (reservoir: 4.8 m/m %; caprock: 9.4 m/m %) and plagioclase (reservoir: 0.9 m/m %; caprock: 1.9 m/m %).

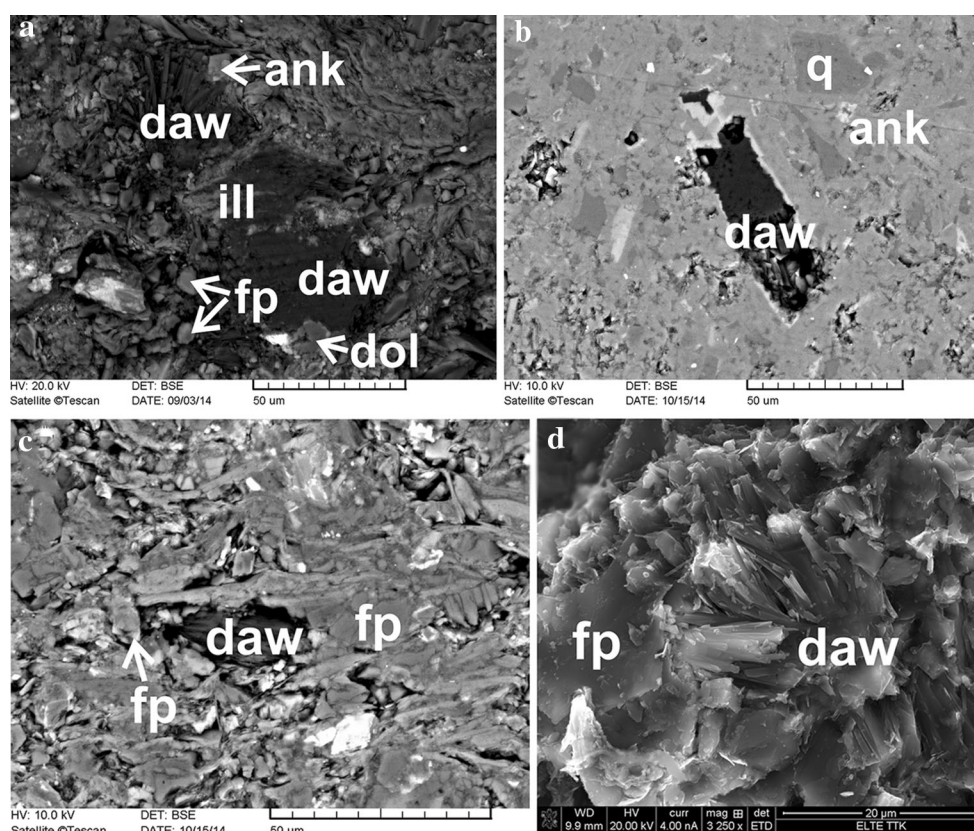
The FTIR results are in agreement with the outcomes of the XRD (Fig. 3a). However, the main importance of the ATR FTIR method in this project is the significantly lower detection limit for dawsonite in the samples compared to XRD. Hence, FTIR results indicate that five samples (RM6-7C, RM6-8BC, RM6-9C, RM46-4/1C and RM46-6B) contain dawsonite (Fig. 3b), in contrast to XRD results that only showed the presence of dawsonite (2 m/m %) in RM6-9C. The fingerprint band of dawsonite is at  $3280 \text{ cm}^{-1}$  (Serna et al. 1985), whereas the bands of clay minerals are usually between  $3500$  and  $3700 \text{ cm}^{-1}$  in the ‘hydroxyl region’ with FTIR (Farmer 1974; Madejová and Komadel 2001).

### Discussion

To understand the behaviour of  $\text{CO}_2$  in a potential  $\text{CO}_2$  storage site, study of the leak-proof natural  $\text{CO}_2$  occurrences is essential because in these systems the  $\text{CO}_2$  is present for geological timescales (Mészáros et al. 1979; Stevens et al. 2006; Kaldi et al. 2011). Therefore, it can be assumed that even long term geochemical reactions in the brine— $\text{CO}_2$ —caprock system have taken place. The geological structures that are analogous to the natural  $\text{CO}_2$  occurrences are supposed to be adequate for safe industrial  $\text{CO}_2$  storage (Pearce et al. 1996).

In natural  $\text{CO}_2$  storage systems the physico-chemical properties of caprocks are less studied than the reservoirs, furthermore most of the studies dealing with caprock lithologies focus only on the petrophysical properties of caprocks (e.g. trend effective porosity, permeability, grain size) (Stevens et al. 2006; Kaldi et al. 2011). Our results indicate that the geochemical and mineralogical analysis is





**Fig. 2** Scanning electron microscope images, where **a**, **b** and **c** images are back scattered electron images, and **d** is a secondary electron image. **a** Dawsonite associated with illite, relict feldspar (albite), diagenetic ankerite, dolomite and quartz; **b** Matrix of the RM46-4/1C sample consisting of ankerite and quartz; dawsonite is seen in a secondary pore, which may have been feldspar according to the morphology of the secondary pore; **c** albite relicts occurring in

intimate relationship to diagenetic dawsonite. Where albite is unaltered dawsonite is not present; **d** fibrous dawsonite crystal in association with feldspars, mica and ankerite. *fp* feldspar, *daw* dawsonite, *ill* illite, *ank* ankerite, *dol* dolomite, *q* quartz, *ms* muscovite. FIB-SEM image and reconstruction courtesy of Zoltán Dankházi and Faculty of Science Research and Instrument Core Facility at Eötvös University Budapest, Hungary

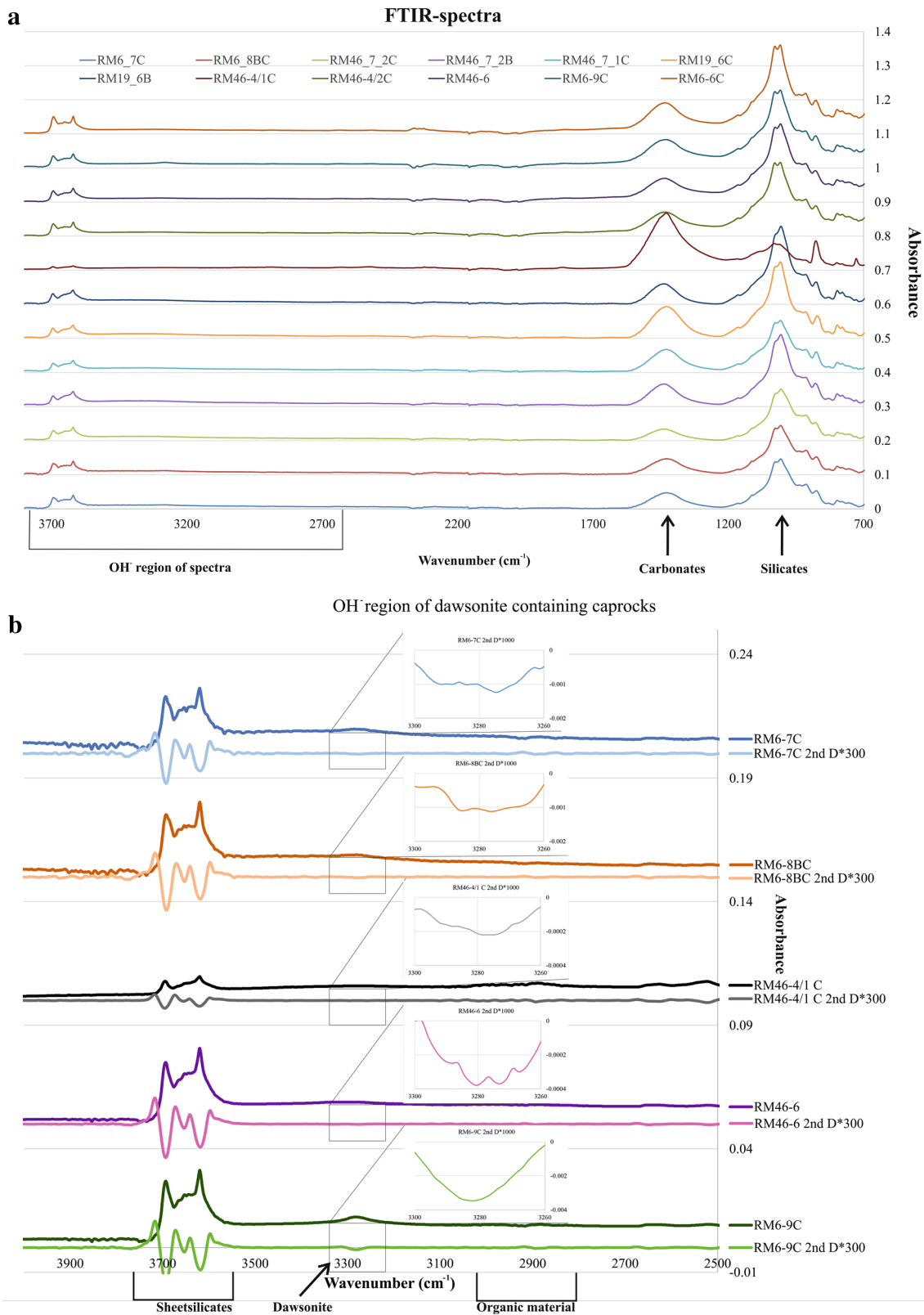
**Table 3** Results of XRD analyses of the studied caprocks, and the average mineral composition of the related reservoirs (Király et al. 2016)

Minerals	Average (m/m %)	Min (m/m %)	Max (m/m %)	Average modal composition in reservoir sandstones (m/m %)
Illite	8	0	22	1.8
Muscovite	15.3	0	26	12.1
Kaolinite	8.5	0	14	10.7
Quartz	29.2	10	44	46.6
K-feldspar	1.5	0	5	1.2
Plagioclase (albite)	1.9	0	6	0.9
Calcite	9.4	0	18	4.8
Dolomite+ankerite	20.3	10	77	16.1
Siderite	3.3	0	16	2.9
Others	5.85			3.1

also vital. According to XRD, ATR FTIR and SEM results (Table 3; Figs. 2, 3), the caprock of a system thought to be leak-proof can also react with CO<sub>2</sub>. The applied analytical methods, however, are essential to reveal the occurrence of these reactions.

### Quality of the caprocks

The most important nature of a caprock to retain CO<sub>2</sub> in the underlying reservoir is its low permeability (Kaldi et al. 2011). Based on the well-log interpretation, the studied



**Fig. 3** spectra of ATR FTIR, where  $x$ -axis is the wavenumber,  $y$ -axis is the absorbance, 2nd D is the second derivate of the spectra. **a** Total spectra of ATR FTIR from all studied samples are shown. **b** The OH<sup>-</sup>

region of the spectra of ATR FTIR are shown from the dawsonite-bearing caprock samples (RM6-9C, RM46-6, RM46-4/1C, RM6-8BC, RM6-7C)

caprocks of the Mihályi-Répcelak field natural CO<sub>2</sub> reservoir have low trend effective porosity ( $\sim 4\%$ ) (using Eq. 3), permeability ( $\sim 0.026$  mD) (using Eq. 4) and high clay content ( $\sim 79\%$ ) (using Eq. 2). The calculated clay content is very similar to the quantity of the measured silt fraction ( $79.9 \pm 5\%$ ) (Table 2). According to the Quantitative Risk and Decision Analysis Tool for Caprock Integrity factors (QRDAT), the permeability of these caprocks is in the moderate risk group (1–0.001 mD) (Bruno et al. 2014). Furthermore, we compared the recent results from the Mihályi-Répcelak area with the Eau Claire Formation (Illinois, USA) (KunleDare 2005). This formation is lying over the Mount-Simon Sandstone Formation and is the caprock of the reservoir that is used to store injected industrial carbon-dioxide (KunleDare 2005; Griffith 2012).

The well-log geophysical results indicate (Table 1) that our studied caprocks show strong similarities in their geophysical properties (porosity:  $\sim 4\text{--}5\%$ , permeability: 0.076–0.001 mD) to the Eau Claire Formation where the porosity is  $\sim 3\text{--}4\%$  (Streibel et al. 2014) and the permeability 0.0014–0.00067 mD as reported by Birkholzer (2009), Person et al. (2010) and Bonneville (2013). The conclusion, based on the calculated parameters, is that geophysical data support the well-sealing characteristics of the caprocks in the Mihályi-Répcelak area.

### Effect of CO<sub>2</sub> on the caprocks

All studied samples are siltstones according to the analysis of grain size distribution (Table 2), furthermore, the XRD results show that the mineral composition of the caprocks in general is similar to that of the reservoirs (Király et al. 2016). A new analytical routine that includes ATR FTIR, among other conventional phase analytical tools like XRD and SEM, have the capability to indicate whether caprocks reacted with CO<sub>2</sub> or not as long as at least trace amounts of dawsonite has formed during the reaction. The results of ATR FTIR (Fig. 3b) indicate the presence of dawsonite in several caprock samples from the study area. Furthermore, the SEM studies in the dawsonite bearing samples shed light on dawsonite-forming mineralogical reactions clearly related to the presence of CO<sub>2</sub> (Fig. 2a–d). Dawsonite occurs either in the close vicinity of albite relicts (Fig. 2a, c, d) or is located in secondary pores which resemble the morphology of former feldspars (albite) (Fig. 2b). These results are not unexpected in the studied rocks because the modal composition of the reservoir sandstones resembles that of the caprocks (Table 3).

Kiraly et al. (2016) showed that the CO<sub>2</sub> containing reservoir sandstones in the studied field are rich in dawsonite (1–16 m/m %). The dawsonite-forming mineral reactions are suggested to be related to the presence of CO<sub>2</sub>. We assume that the studied caprocks are affected by similar mineral reactions. However, these reactions are localized

processes in the caprocks, because the flow rate of the reactive fluid, namely CO<sub>2</sub> saturated brine (Liu et al. 2012) is limited due to low permeability of caprocks.

The dissolution of such minerals as plagioclase, carbonates, mostly calcite, ankerite, siderite, could cause local oversaturation and exsolution of specific phases mainly carbonates, mostly dawsonite and ankerite, in the secondary pores. Our results show that the CO<sub>2</sub> saturated brine not only migrates into the caprock but the CO<sub>2</sub> saturated pore water also reacts with minerals of the caprocks. Consequently, the physical properties of caprock (porosity and permeability) may change, however, the direction and degree of these changes are currently unknown. In most experimental studies (e.g., Berthe et al. 2011) the containment properties of the caprocks were degraded after the reactions. As a result of mineralogical and physical changes the CO<sub>2</sub> retainment capability and, therefore, the suitability of the caprocks may be compromised. On the other hand, the SEM and FTIR results (Figs. 2, 3) show that the CO<sub>2</sub> entering the caprocks may be trapped in the mineral phase of the caprock through mineral CO<sub>2</sub> pore water reactions described above. This implies that even if CO<sub>2</sub> can migrate into the caprock, either as a free phase or dissolved in the brine, at least some of it will react and be stored in the sealing lithology as a mineral phase (e.g. dawsonite), increasing the total storage capacity of the given storage site.

### Detection limit of FTIR

The detection limit of infra active phases (hydroxyl, molecular water, etc.) using ATR FTIR may be much lower than the detection limit of XRD ( $\sim 0.1\text{--}1$  m/m %); (Cook et al. 1975). The potential detection limit of dawsonite measured by ATR FTIR methodology can be estimated based on its hydroxyl content (12 m/m % in ‘water’ equivalent) manifested as the band at  $3280\text{ cm}^{-1}$  in the infrared spectra (Serna et al. 1985). Given that the ATR FTIR may be able to detect as low as 0.01 m/m % structural hydroxyl (Madejová and Komadel 2001) and dawsonite contains 12 m/m % hydroxyl this ideally corresponds to  $\sim 0.083$  m/m % tentative detection limit for dawsonite. This suggests that ATR FTIR may have higher sensibility to the presence of dawsonite than XRD. This is clearly reflected in our results as ATR FTIR still indicates the presence of dawsonite in samples in which XRD does not support the occurrence of this mineral.

### Conclusions

The Mihályi-Répcelak natural CO<sub>2</sub> occurrence is suggested to be a leak-proof field, furthermore, based on well log data and production history, the sealing properties of caprocks are suitable on geological time scale. According to our studies, the following conclusions can be drawn:



1. Despite the lack of surface or near surface occurrence, CO<sub>2</sub> migrates in (and probably through) the well-sealing caprocks in the study area over geological timescales. However, it is retained within the storage formation.
2. The geochemical effect of CO<sub>2</sub> saturated brine is similar in the clayey caprocks and in the reservoir sandstones, however, the CO<sub>2</sub>—brine—caprock reactions are much more localized and less pervasive in the caprocks. The reason of this may be the low permeability (~0.026 mD) of the caprocks, the flow of CO<sub>2</sub> saturated fluid is slow.
3. Using multiple analytical techniques with special emphasis on the ATR FTIR technique, we have demonstrated that dawsonite is present in several studied samples as a product of the CO<sub>2</sub>—brine—caprock reactions.
4. Caprocks of natural CO<sub>2</sub> occurrences, and future industrial storage sights, should also be thoroughly studied because the CO<sub>2</sub> can migrate even through well-sealing caprocks. During its migration CO<sub>2</sub> may react with minerals in the caprock, which could significantly affect original caprock properties and their capabilities in retaining CO<sub>2</sub> in the reservoir.
5. According to our results, the caprock not only behaves as a physical barrier but can also trap the CO<sub>2</sub> in the minerals such as dawsonite. This implies that the caprock may not only physically retain injected CO<sub>2</sub> but may also behave as a geochemical trap which could improve the safety of the storage system.

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