

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

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ABSTRACT

Natural CO₂ reservoirs provide an opportunity to study long-term fluid-rock interactions, which are essential to reassure the safety of mineral storage of carbon-dioxide. The Mihályi-Répcelak field (Pannonian Basin, Central Europe) is one of the largest natural CO₂-bearing reservoirs in Europe (25 Mt). The CO₂ was trapped in Neogene sandstones, which contain various carbonate minerals (dolomite, ankerite, siderite, dawsonite). To reveal the origin of the parent fluid, from which these minerals precipitated, dawsonite and siderite were separated by a new physical method to minimise the uncertainties in the analysis of their stable isotope composition. The $\delta^{13}\text{C}_{\text{Daw}}$ values range from +1.3‰ to +1.6‰ and the calculated $\delta^{13}\text{C}_{\text{CO}_2}$ values in equilibrium with dawsonite (−4.8‰ - −2.0‰) overlap with the carbon isotope compositions of the local CO₂ and the European Subcontinental Lithospheric Mantle (−3.9‰ - −2.1‰). This indicates that the dawsonite-forming CO₂ had a magmatic origin. The siderite data indicates that some formed from the magmatic CO₂, possibly simultaneously with dawsonite (−6.0‰ - −3.9‰), whereas the rest (−8.4‰ - −6.1‰) formed either from a fractionated CO₂ with magmatic origin or before the CO₂ invasion. The hydrogen isotope composition of structural OH[−] of dawsonite (−57‰ to −74‰) was determined and was used to estimate the origin of the interacting porewater. The calculated porewater data (δD : −69‰ - −103‰ and $\delta^{18}\text{O}$: −1.4‰ - +4.7‰) indicate that the parent fluid was meteoric water modified by water-rock interaction. Our data allows estimation of the total amount of CO₂ stored in the dawsonite-bearing sandstone reservoir to be 25 kg/m³, well in line with previous modelling works, which gives a total of 2.01 × 10⁶ t of CO₂, higher than previous estimates.

We suggest that individual mineral analysis complemented by hydrogen isotope analysis is to be employed to effectively trace in-reservoir fluid-rock interactions in CO₂ reservoirs and provide valuable input data for geochemical modelling for better predicting conditions for mineral storage of CO₂.

1. Introduction

The constant increase in atmospheric carbon-dioxide (CO₂) concentrations related to anthropogenic emissions gains special importance

with respect to global climate change. ‘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 found (IPCC, 2005, 2013).

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Mineral storage of carbon-dioxide is one of the most promising ways of storing CO₂ safely underground. A number of different host rocks such as basalts and ultramafic rocks (Matter et al., 2016; Pogge von Strandmann et al., 2019; Snæbjörnsdóttir et al., 2020), sandstones (Worden, 2006) and carbonates (Stevens and Tye, 2007) have been investigated for this purpose. Although these results may be adapted to the long-term storage of CO₂, upscaling of these experiments to the industrial level (Gt CO₂ injection/annum) faces difficulties. 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 time (e.g. Baker et al., 1995; Gao et al., 2009; Gilfillan et al., 2009; Király et al., 2016a; Pearce et al., 1996).

When a large amount of CO₂ floods a sandstone reservoir, the dynamic equilibrium between porewater and rocks is likely to be shifted. Firstly, CO₂ will be trapped in the pores via structural trapping, then it will dissolve in the porewater (solubility trapping) (Bachu et al., 2007; Bickle et al., 2013; Oelkers et al., 2008), which will cause the drop of reservoir fluid pH. As a result, carbonates and aluminosilicates will start dissolving and other carbonates and clay minerals will (re)precipitate. Most geochemical models from sandstone reservoirs and CO₂ injection fields predict the 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; Xu et al., 2003, 2005). Dawsonite formation has been presented in studies on natural CO₂ reservoirs worldwide, and it has been explained by a response to CO₂ flooding (Baker et al., 1995; De Silva et al., 2015; Gaus, 2010; Király et al., 2017; Xu et al., 2003; Zhou et al., 2014).

The Mihályi-Répcelak area in the Pannonian Basin (NW-Hungary) contains ~25 million tons of CO₂ in sandstone formations (Mészáros et al., 1979) and is one of the largest CO₂ producing gas fields in Europe. The formation in which the reservoir developed is widespread in the Pannonian Basin and it has been identified as prosperous for large-scale CO₂ storage (Falus et al., 2011). Previous studies showed that a significant amount of dawsonite is present in some of the reservoirs of the Mihályi-Répcelak area along with ankerite that may have crystallized simultaneously to and after dawsonite (e.g. Király et al., 2016a). This petrographic observation combined with the presence of magmatic CO₂ (Nádor, 2002; Palcsu et al., 2014; Vető et al., 2014) provides an excellent opportunity to study the diagenetic minerals, formed before and after the CO₂ inflow, by isotope geochemical means.

The isotope geochemistry of carbonate minerals has been used to determine the origin of fluids where carbonates precipitated from, and to evaluate the processes that take place both in natural CO₂ reservoirs (Baker et al., 1995; Gao et al., 2009; Liu et al., 2011; Zhao et al., 2018) and in CO₂ injections (Higgs et al., 2015; Stevens and Tye, 2007; Worden, 2006). Most of these studies used the carbonate stable isotope composition inferred from the bulk rock measurements (e.g. Liu et al., 2011; Zhao et al., 2018).

In this study, we focus on the Mihályi-Répcelak area and use the C and O stable isotope values of carbonates obtained from separated minerals instead of measuring bulk samples. In addition, we report the H isotope values of dawsonite to determine the source of the fluid from which the mineral formed. These technique together likely provides more confidence in how certain mineral phases have formed and allows

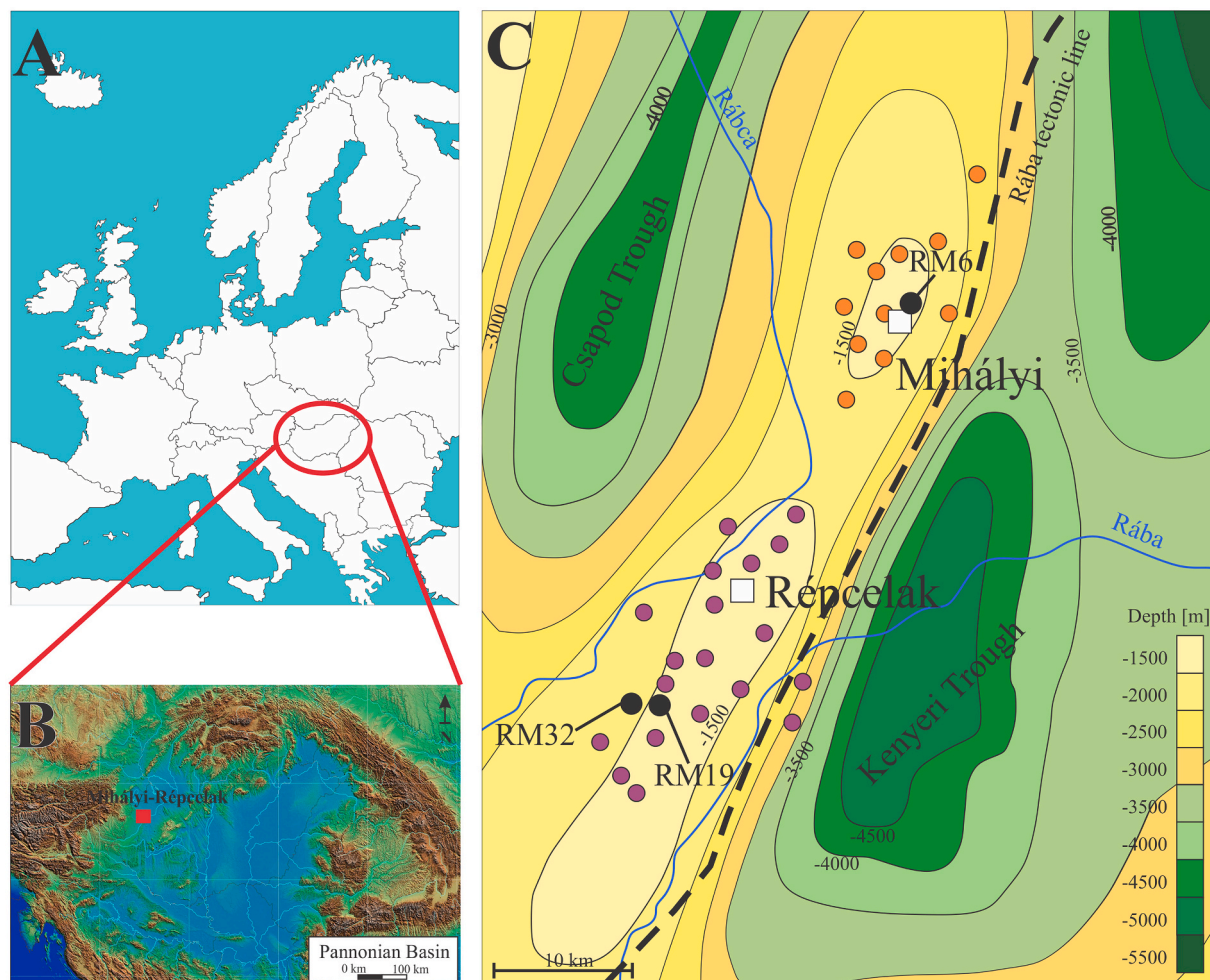


Fig. 1. Location of study area in Europe (A), in the Pannonian Basin (B) and the study area (modified after Zilahi-Sebess, 2013) showing the studied boreholes (C).

a better constraint on local conditions on mineral storage of carbon-dioxide.

2. Geological setting

The study area is located in the western part of the Pannonian Basin in Hungary, bordered by the Csapod Trough from the west, and the Rába tectonic line from the east. The area consists of two parts Mihályi and Répcelak field (Fig. 1) which are located 17 km from each other. The Mihályi reservoirs are deeper (~1200–1650 m) than the Répcelak counterparts (~1150–1450 m) but they are hydrologically connected (e. g. Palcsu et al., 2014). The area started filling up 10–9 Ma ago in the Lower Pannonian (Tortonian) with sediments of a prograding delta system (Juhász, 1992) forming a several km thick fluvial sedimentary sequence. It starts with alternating marl and claymarl sediments (Endrőd Formation), followed by a turbiditic sandstone (Szolnok Formation). This is followed by dominantly siltstone layers (Algyő Formation) with sandstone interbeddings. The Upper Pannonian sequences are alternating siltstone, sandstone and claystone successions (Újfalu and Zagyva Formations). Volcanic activity has been described close to the study area in the Pliocene (Jugovics, 1970; Wijbrans et al., 2007). The basin entered the oil window during the Late Miocene (8–7 Ma) and oil traces and gas (mostly CH₄) accumulations have been found in the area (Mészáros et al., 1979). The genetic link between oil and CH₄ has been established by stable isotope geochemistry (i.e. carbon isotope ratio of CH₄ and the whole oil residue, Koncz and Etler, 1994). A mixture of CH₄-N₂ has been migrating to the Pannonian Formations from Silurian metasediments (Csizmeg et al., 2012; Vető et al., 2014). Most of the CH₄ has been exploited for industrial purposes and the reserves were considered as depleted ones (Vető et al., 2014).

The whole area has been studied since 1930s with various geophysical (both gravity and seismic) methods and CO₂ was found but the detailed investigation for natural gas reserves started in the 1960s (Mészáros et al., 1979; Kőrössi, 1987). According to recent research (Palcsu et al., 2014; Vető et al., 2014), the CO₂ inflow occurred during the Late Miocene/Early Pliocene. In the two study areas, a total of 26 vertically stacked CO₂-bearing reservoirs are hosted in the Algyő and Újfalu Formations at the depth of 1300–1600 m (Mészáros et al., 1979). This natural CO₂ was trapped in the sandstone bodies interbedded with the clayey/siltstone layers that have prevented CO₂ migration to the surface (Király et al., 2016b).

The origin of CO₂ accumulated in the studied sedimentary sequence has been a matter of debate. Koncz (1983) assumed metamorphic or volcanic/magmatic origin for CO₂ based on measured $\delta^{13}\text{C}_{\text{CO}_2}$ values (range between -7.0‰ and -4.0‰). Cornides et al. (1986) further studied the well gases. The measured carbon and helium isotope ratios ($\delta^{13}\text{C}_{\text{CO}_2} = -6.5\text{‰}$ to -5.2‰ , $^3\text{He}/^4\text{He}_{\text{max}} = 3.93 R_A$, where R_A is the atmospheric ratio of 1.399×10^{-6} , Mamyrin et al., 1970) indicated that the CO₂ has probably mantle origin, which is in line with typical magmatic derived isotopic ratio ranges (-8‰ - -4‰) (Ohmoto and Rye, 1979; Győre et al., 2015). Additionally, the CO₂ measurements of Nádor (2002) ($\delta^{13}\text{C}_{\text{CO}_2} = -5.5\text{‰}$ - -3.1‰) also agrees with this assumption. Based on the petrographic and geochemical studies, two phases of volcanic activity, Pásztori volcano (12–10 Ma) and Kemesalja (6 Ma) occurred in the vicinity of the study area (Harangi et al., 1995; Jugovics, 1970; Tari, 1994). According to the K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ ages, the volcanoes formed between 5.5. to 4.2 Ma (Balogh et al., 1982, 1986; Wijbrans et al., 2007). Most recently, a comprehensive stable and noble gas isotope study from the Mihályi-Répcelak field also confirmed that most of the CO₂ has mantle origin based on, among others, $\delta^{13}\text{C}_{\text{CO}_2} = -3.3\text{‰}$ - -2.1‰ and $\text{CO}_2/{}^3\text{He} = 2.17 \times 10^8$ – 3.38×10^{10} (Palcsu et al., 2014). In addition, these observed $\delta^{13}\text{C}_{\text{CO}_2}$ values agree well with those proposed for the European Subcontinental Lithospheric Mantle (SCLM) (-3.9‰ - -2.1‰) based on the detailed investigation of the Eger rift (Weinlich et al., 1999). Palcsu et al. (2014) and Vető et al. (2014) concluded that the CO₂ originates from degassing melts ascending from the

asthenosphere. The CO₂ probably migrated along the Rába tectonic line towards the Mihályi-Répcelak area, where it has accumulated in the Pannonian sediments (Kőrössi, 1987).

3. Samples and methods

3.1. Sample selection

From the Mihályi and Répcelak fields six sandstone reservoirs out of the 26 (Fig. 1) contain dawsonite (Király et al., 2017), which were selected for this study. Four samples (7R1, 7R2, 7R3, 9R) derived from the RM6 drill core from the Mihályi field (1419–1461 m; 98% CO₂, Mészáros et al., 1979). Sample 6R (1396–1415 m, 96% CO₂) and 5R2 (1375–1392 m, 90% CO₂) were selected from RM19 and RM32 drill cores, respectively, from the Répcelak field (Mészáros et al., 1979). All samples, except RM6-9R and RM32-5R2, are from CO₂ reservoirs currently under operation by Linde Gas Hungary.

3.2. Mineral association and petrography

Mineral associations were determined by X-ray diffraction analysis (XRD) on bulk rock powders (<63 μm) at the MBFSZ (Budapest, Hungary), using a Phillips PW 1730 X-ray diffractometer. Petrographic features of selected sandstone samples were characterized by optical microscopes and AMRAY 1830 I/T6 scanning electron microscope (SEM) coupled with EDAX PV 9800 energy dispersive X-ray spectrometer, and Hitachi TM4000 Plus AztecOne EDS (15 kV, 0.8 nA) at ELTE (Budapest, Hungary). Optical determination of mineral modes was carried out on backscattered electron images with 300 points per image following the technique established by Király et al. (2017). Applying this technique, we also calculated the relative amount of the different carbonate minerals (calcite, dolomite, ankerite+siderite and dawsonite) and also determined by XRD.

3.3. Stable C and O isotope compositions

The different carbonates show a highly complex petrography. The interpretation of the stable isotope data of individual carbonate minerals is not straightforward when the selective dissolution technique established by McCrea (1950), Baker et al. (1995) and Liu et al. (2011) is applied. This is because of the overlapping dissolution profiles of the different carbonates. For this reason, in this study a new method was applied to disintegrate the rock samples, which allows physical separation of dawsonite and siderite from each other and from other carbonates, to determine their isotopic compositions individually. Due to textural reasons, the other carbonates could not be separated from each other.

First, rock samples were disintegrated by H₂O freezing-melting cycles. The advantage of this method, compared to crushing, is that the majority of minerals preserve their original grain size, shape and habit which helps their separation. Following disintegration, wet sieving was carried out producing grainsize fractions: >250 μm, 250–63 μm, <63 μm. Then, dawsonite grains were separated by hand picking from the 250–63 μm size fractions from samples RM6-9R and RM32-5R2 having the highest modal content of dawsonite (see Section 4.1) under stereomicroscope. Under the stereomicroscope, dawsonite is easily distinguishable from the other carbonates because dawsonite is the only white fibrous mineral phase in the samples. We used the same size fractions (250–63 μm) for siderite separation, applying Frantz Isodynamic Magnetic Separator (0.6 A magnet current, Parfenoff et al., 1970) at MBFSZ (Budapest, Hungary) from samples RM6-7R1, RM6-7R3, RM6-9R, RM19-6R. The purity of the separates depends on the mineral composition of the host rock and the quality of the mineral grains (Strong and Driscoll, 2016). Therefore, we checked the success of the magnetic separation under stereomicroscope (siderite has an orange colour and isometric grain shape) and also with SEM (Hitachi TM4000 Plus

AztecOne) at ELTE (Budapest, Hungary).

Stable carbon and oxygen isotope compositions were determined on 150–200 µg of carbonate powders (prepared from the mineral separates) by reacting the powders with orthophosphoric acid at 72 °C for 1 h for

dawsonite and for 24 h for siderite (Spötl and Vennemann, 2003). We analysed the separated CO₂ using an automated GASBENCH II sample preparation bench attached to Thermo Finnigan Delta Plus XP Isotope Ratio Mass Spectrometer (IRMS) at IGGR (Budapest, Hungary). Acid

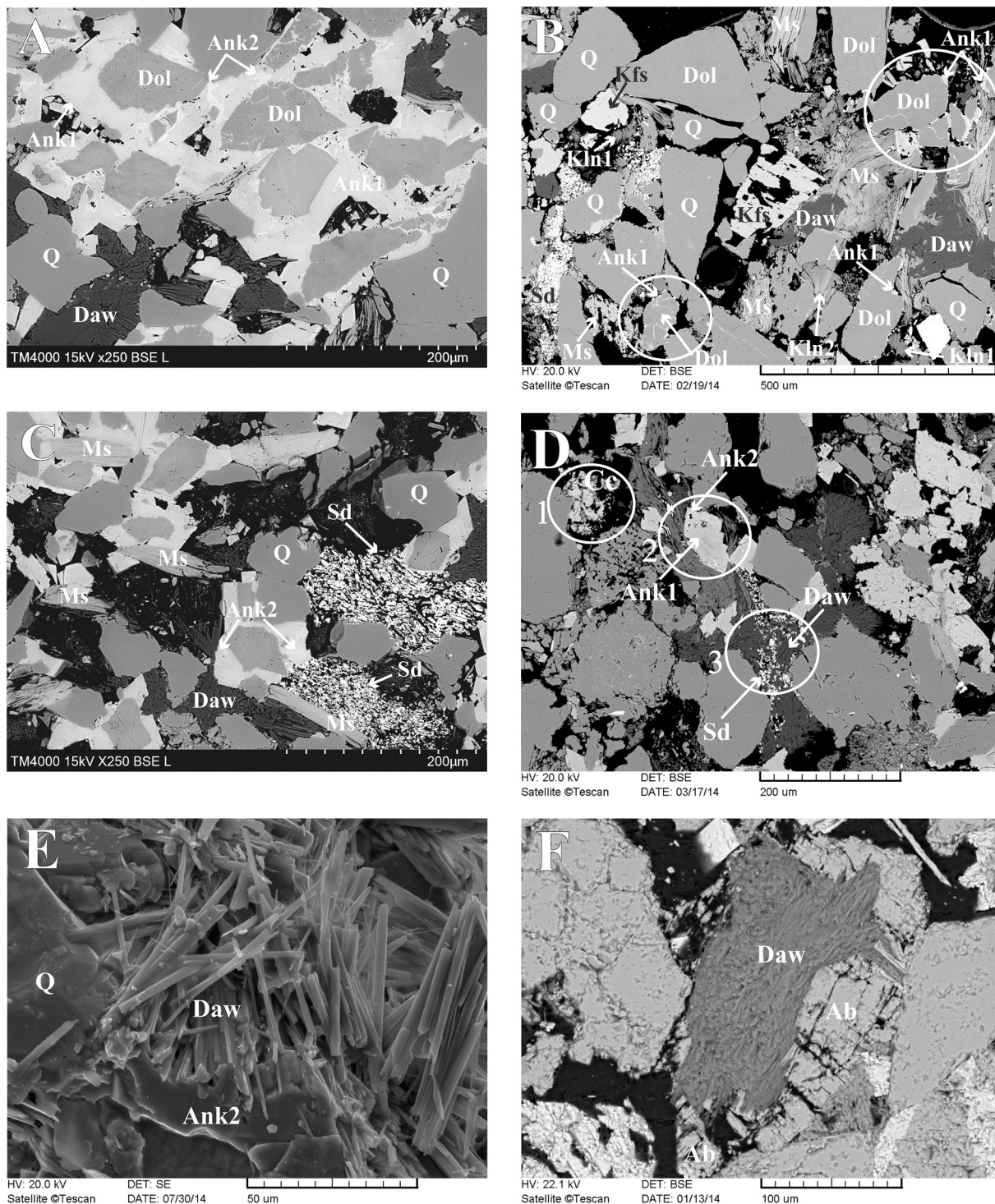


Fig. 2. Backscattered (A–D and F) and secondary (E) electron image of dawsonite-bearing sandstones from the Mihályi-Répcelak area, Hungary. A: Ankerite is present in two generation rims Ank1 (early) and Ank2 (late) around the dolomite (Dol). B: Ank1 shows rudimentary feature on dolomite. C: Ank2 is in close textural relation with dawsonite (Daw), siderite (Sd) forms large patches. D: Area-1 indicates dissolution of calcite (Cc). Area-2 shows relation of early (Ank1) and late (Ank2) as sign for generation of zoned ankerite cement. Area-3 shows textural relation for simultaneous formation of siderite (Sd) and dawsonite (Daw). E: Assemblage of Dawsonite (Daw), quartz (Q) and ankerite (Ank2) suggesting coeval formation. F: Albite (Ab) dissolution and dawsonite (Daw) precipitation. Abbreviations: Ank1: ankerite with low FeO + MnO content, Ank2: ankerite with high FeO + MnO content, Daw: dawsonite, Dol: dolomite, Sd: siderite, Ab: albite, Kfs: K-feldspar, Kln1: early generation of kaolinite, Kln2: late generation of kaolinite, Ms.: muscovite, Q: quartz.

fractionation factors determined by Rosenbaum and Sheppard (1986) and Kim et al. (2007) were applied for siderite and dawsonite, respectively (the fractionation factor for calcite was also applied to dawsonite in other studies, e.g. Baker et al., 1995; Liu et al., 2011). The isotopic compositions are expressed as $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (in ‰) relative to V-PDB and V-SMOW, respectively (Coplen, 1996). Three laboratory standards (calibrated against NBS-18, NBS-19 and LSVEC) provided by the International Atomic Energy Agency were applied for standardization (Flesch et al., 1973; Friedman et al., 1982). A Harding Iceland Spar (Landis, 1983) sample was measured as an unknown, and yielded $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of $-4.84 \pm 0.05\%$ and $-18.56 \pm 0.07\%$ ($n = 24$), respectively. These values are within error of the published values of -4.80 and -18.56% , respectively (Landis, 1983). On the basis of these results and measurement reproducibility, the accuracies of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are estimated to be better than $\pm 0.1\%$.

3.4. Stable H isotope compositions

Stable hydrogen isotope composition of the hydroxyl group of dawsonite ($\text{NaAlCO}_3(\text{OH})_2$) was determined using an LGR LWIA-24d type laser analyser attached to an in-house built inlet system at IGGR (Czuppon et al., 2014; Demény et al., 2016). Bulk rock samples (250–63 μm fraction) containing dawsonite were heated up to 350°C to release the OH^- group (Földvári, 2011). The liberated fluids (H_2O and CO_2) were trapped in a liquid nitrogen-cooled cold finger. The trapped CO_2 was liberated at -80°C (using melting Ethyl alcohol) and removed from the system, and then the H_2O was liberated at 80°C and introduced into the laser analyser. Using bulk rock sample in this instance is reasonable because the only other OH^- -bearing mineral (kaolinite) presents decomposes thermally as high as 580°C (Földvári, 2011), leaving it intact at the above temperature. The isotopic compositions are expressed as δD values relative to V-SMOW (Coplen, 1996), the reproducibility of the measurements is estimated to be $\pm 2\%$ based on synthetic dawsonite analyses.

In order to confirm that entire OH^- was released from dawsonite during the hydrogen isotope analyses, we investigated the OH-content by a Bruker Vertex 70 Fourier-transformation infrared spectrometer (FTIR) equipped with a Bruker Platinum diamond ATR cell at MBFSZ (Budapest, Hungary). The disappearance of the O–H related band of dawsonite at 3280 cm^{-1} (Király et al., 2016a) on the FTIR spectra of the residual sample confirmed the complete elimination of dawsonite OH^- group after the hydrogen isotope measurement.

4. Results

4.1. Petrography of dawsonite-bearing sandstones

The petrography of our samples was described earlier (Király et al., 2016a; Király, 2017) which can be summarized as follows: The dolomite is the only carbonate, which most likely represents original detrital grains. The ankerite can occur as a pore filling material, cement, mineral replacement (as a rim around dolomite) and overgrowth (Fig. 2A). This mineral was determined as the most common diagenetic carbonate. In

some cases, the ankerite rims has incipient features in the rocks (RM19-6R, RM6-7R1, RM6-7R2, RM6-7R3; Fig. 2B). The amount of the diagenetic/detrital carbonate ratios vary between the samples.

Our samples contain 72–74 v/v% quartz (Q), 2–6 v/v% feldspar (F) and 15–25 v/v% lithoclast (L) based on the McBride (1963) QFL classification. Accordingly, the studied samples are sublitharenites. The only exception is RM32-5R2 sample, which contains 83 v/v % quartz. The ratio of detrital versus diagenetic carbonate (detr/diag) were also determined for each sample. The lowest ratios (1:5.3) were found in the RM6-9R sample, where the detrital carbonates (dolomite) are 7 w/w% and the diagenetic carbonates (ankerite, calcite, dawsonite, siderite) are 37 w/w% (Table 1). The highest ratios (1:1.1) were observed in the RM19-6R sample, where the detrital carbonates are 7 w/w% of the total mineral modes whereas the diagenetic carbonates are 8 w/w% (Table 1).

In those samples where dawsonite is around 8–16 w/w%, the ankerite rims occur in two generations. The generations differ in their FeO + MnO contents with ~ 10 w/w % and ~ 18 w/w %, respectively. Late generation ankerite can be found along the cracks of the early ankerite and dolomite (Fig. 2A). Based on the petrographic observations, dawsonite and late generation of ankerite (i.e. the outer rims) are in close textural relationship (Fig. 2C). Calcite grains (RM6-7R1, RM6-7R2, RM6-7R3, RM32-5R2) are rare and occur in the pores of the sandstones and often show dissolution features (Fig. 2D). Siderite appears as a pore filling, fine grained carbonate and as a pseudomorph of silicates (probably biotite, Fig. 2B). Siderite also appears in iron rich clayey clast (RM6-7R3) and as continuous thin layers in large ($\sim 200\ \mu\text{m}$) patches in the dawsonite-bearing sandstones (RM6-9R, Fig. 2C). Solely, sample of RM32-5R2 does not contain siderite (Table 1). Dawsonite occurs as a fibrous, pore filling minerals. Dawsonite is present in close textural relation with ankerite, kaolinite and quartz overgrowths (Fig. 2E). We also observe dawsonite replacing partially dissolved albite (Fig. 2F).

4.2. Stable carbon and oxygen isotope compositions of separated carbonate minerals

The $\delta^{13}\text{C}$ values of dawsonite ($\delta^{13}\text{C}_{\text{Daw}}$) vary between $+1.5\%$ and $+1.3\%$, whereas the $\delta^{18}\text{O}_{\text{Daw}}$ values range from $+19.5$ to $+22.2\%$ (Table 2). In contrast, the stable isotope compositions of siderite show larger variation defining two generational different groups. The $\delta^{13}\text{C}_{\text{Sd}}$ and $\delta^{18}\text{O}_{\text{Sd}}$ values of Group-1 range from $+4.2$ to $+4.3\%$ and from $+24.8$ to $+25.1\%$, respectively. Both the carbon and oxygen isotope compositions of Group-2 are characterized by lighter values ($\delta^{13}\text{C}_{\text{Sd}}$: from $+1.3$ to $+2.1\%$; $\delta^{18}\text{O}_{\text{Sd}}$: from $+22.2$ to $+22.3\%$; Table 2).

4.3. Stable hydrogen isotope composition of dawsonite-bearing sandstones

The determined δD values of dawsonite-bearing samples from the Mihályi field cover a narrow range between -61% and -59% (Table 2), except for one sample (RM6-9R) that shows a lighter value (-74%). The hydrogen isotope composition of dawsonites from the Répcelak field ranges between -62% and -57% .

Table 1

Mineral composition of dawsonite-bearing sandstones refined with the 300 points per image counting. Values are expressed in w/w %. 1 sigma uncertainty is 1%. BDL: below detection limit.

Area	Sample	Calcite	Dawsonite	Dolomite	Ankerite + Siderite	Quartz	Muscovite + Illite	Kaolinite	K-feldspar
Mihályi	RM6-9R	BDL	16	7	21	36	15	3	2
	RM6-7R3	8	4	9	13	43	15	7	1
	RM6-7R2	8	3	6	15	43	16	6	3
	RM6-7R1	10	3	11	10	42	14	9	1
Répcelak	RM32-5R2	<1	8	8	27*	45	8	3	1
	RM19-6R	BDL	3	10	9	52	12	12	2

* sample does not contain siderite.

Table 2

Stable carbon and oxygen isotope compositions of separated minerals (dawsonite, siderite) and stable hydrogen isotope data of dawsonite from the Mihályi-Répcelak area.

Area	Sample	Depth [m]	CO ₂ [v/v %]	δ ¹³ C _{carbonate} [‰, PDB]	δ ¹⁸ O _{carbonate} [‰, PDB]	δ ¹⁸ O _{carbonate} [‰, SMOW]	δD _{dawsonite} [‰, SMOW]	
Mihályi	RM6-9R	1443.5–1461	98	NM	NM	NM	–74	
	RM6-9R Dawsonite-1			+1.6	–11.0	+19.5	NM	
	RM6-9R Dawsonite-2			+1.5	–11.1	+19.5	NM	
	RM6-9R Siderite-1			+2.1	–7.7	+23.0	NM	
	RM6-9R Siderite-2			+1.9	–8.3	+22.3	NM	
	RM6-7R3	1423		NM	NM	NM	–60	
	RM6-7R3 Siderite		+4.3	–5.6	+25.1	NM		
	RM6-7R2	1421.5			NM	NM	NM	–59
	RM6-7R1	1419.5			NM	NM	NM	–61
	RM6-7R1 Siderite		+4.2	–5.9	+24.8	NM		
Répcelak	RM32-5R2	1375–1392	90	NM	NM	NM	–57	
	RM32-5R2 Dawsonite			+1.3	–8.4	+22.2	NM	
	RM19-6R	1394–1415	96	NM	NM	NM	–62	
	RM19-6R Siderite			+1.3	–4.9	+25.9	NM	

CO₂ concentration data are after [Mészáros et al. \(1979\)](#).

Uncertainty of δ¹³C and δ¹⁸O are 0.1‰, δD are 2‰.

NM: not measured.

5. Discussion

5.1. Crystallization and dissolution processes in the reservoir sandstones

One of the most spectacular petrographic features of the sandstone samples from the Mihályi-Répcelak field reservoirs is the complex carbonate association. Based on the textural and chemical characteristics (Table 1 and Fig. 2), the carbonate minerals can be clustered into three genetic groups: 1) detrital, 2) early-diagenetic (formed during the sandstone diagenesis) and 3) late-diagenetic (formed during and after CO₂ flooding). Dolomite most likely represent the detrital carbonate phase that was originally deposited during sedimentation.

Calcite remnants, the low-FeO + MnO ankerites surrounding dolomite and most likely some of the siderites are considered to be early-diagenetic minerals. Calcite, at least, is also partially detrital, whereas siderite is clearly replacing flake-like silicates, presumably biotite and

clay mineral, providing the necessary FeO + MnO for siderite. The low-FeO + MnO ankerite could be the early cement phase in the studied sandstones, partially dissolving dolomite and probably calcite (Fig. 3A). Dawsonite is present in the pores as cement or replacing partially dissolved feldspar (K-feldspar, albite) representing the late diagenetic phase (Fig. 3B). This agrees with the literature on dawsonite formation induced by CO₂ flooding the reservoir (e.g. [De Silva et al., 2015](#); [Worden, 2006](#)). Similar studies elsewhere ([Baker et al., 1995](#); [Fang et al., 2010](#); [Watson, 2012](#); [Zhou et al., 2014](#)) proposed that the source of Na⁺, necessary for the crystallization of dawsonite, came from the dissolving albite or porewater, whereas the source of Al³⁺ came from the dissolution of aluminosilicates (feldspars and clay minerals). We suggest that other carbonates, i.e. the FeO + MnO-rich ankerite and siderite, occurring in the pores in clear textural equilibrium with the pore filling and cementing dawsonites, also formed in relation with the CO₂ flooding event (Fig. 3B).

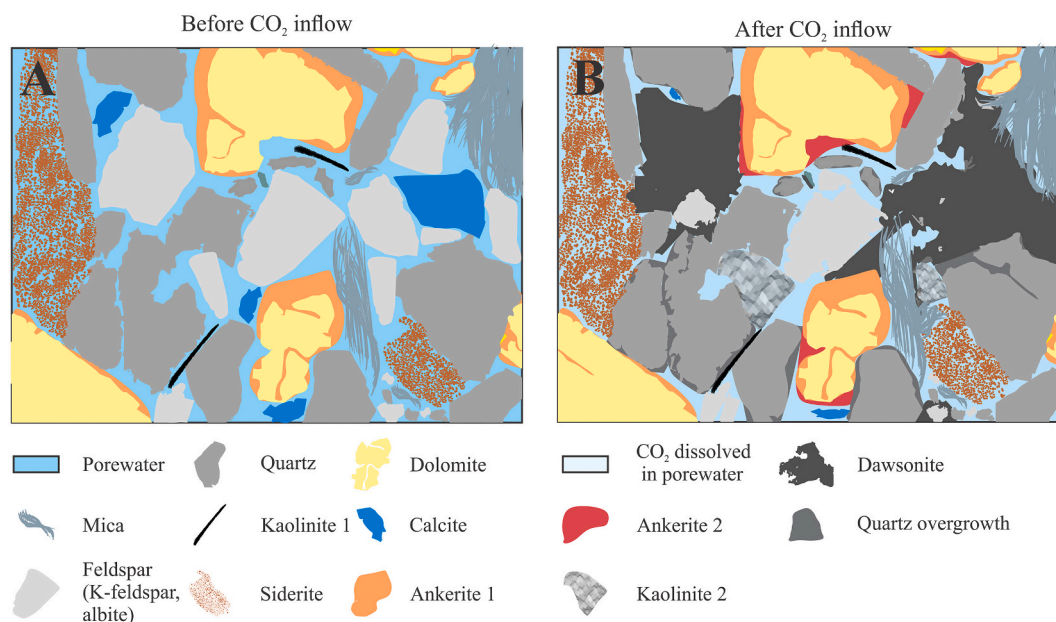


Fig. 3. Schematic ‘snapshots’ of crystallization process before (A) and after (B) the CO₂ inflow in a porewater-sandstone system in the Mihályi-Répcelak field. Due to the dissolution of minerals (e.g. calcite, dolomite, ankerite 1, feldspar, quartz) before CO₂ inflow into the porewater new mineral phases (dawsonite, ankerite 2, quartz overgrowth, kaolinite 2) precipitated in the reservoir. Ankerite 1 with low FeO + MnO content, Ankerite 2 with high FeO + MnO content, Kaolinite 1 is the early generation and Kaolinite 2 is the late generation.

5.2. Origin of the carbonate forming CO₂

In the following section we will constrain the source of the carbonate forming CO₂, using the stable carbon and oxygen isotope compositions of the separated carbonates. We used the measured isotopic compositions of the dawsonite and siderite and applied the carbonate-CO₂ fractionation equations of Bottinga (1968) and Ohmoto and Rye (1979) for dawsonite and Golyshev et al. (1981) for siderite to define the carbon isotope composition of CO₂ that was present during the formation of these carbonates (Eq. S1-S3 in Suppl.). Fractionation factors were calculated for the temperature range of 70 °C and 98 °C, obtained from the geothermal gradient of the Pannonian Basin (40 °C/km; Dövényi et al., 1983; Lenkey et al., 2002), according to the current reservoir depths of 1375–1461 m (as a lower limit at 70 °C) and the assumed reservoir depths (~2100 m) maximum 98 °C before the tectonic uplift (Szamosfalvi, 2014), and an annual average surface temperature of 12 °C. These fractionation factors were used to calculate $\delta^{13}\text{C}_{\text{CO}_2}$ from the Mihályi field (−4.5‰ and −2.0‰) and from the Répcelak field (−4.8‰ and −2.2‰) (Table 3). The calculated $\delta^{13}\text{C}_{\text{CO}_2}$ values in equilibrium with dawsonite (Fig. 4) overlap with those characteristics for the mantle/magmatic derived carbon sources (−8‰ to −4‰; Ohmoto and Rye, 1979) and they agree well with an estimation for the European SCLM ($\delta^{13}\text{C} = -3.9\text{‰} - -2.1\text{‰}$; Weinlich et al., 1999). More interestingly, the calculated $\delta^{13}\text{C}_{\text{CO}_2}$ values also overlap with those ones measured in the free CO₂ gas from the Mihályi-Répcelak field: −5.5‰ - −3.1‰ (Nádor, 2002) and −3.3‰ - −2.1‰ (Palcsu et al., 2014). Note that the reported isotopic composition of CO₂ may differ from the original source because of the mineral forming reactions (isotopic fractionation). Here we assume that the original volume of the CO₂ gas (which may not be limited to the reserve estimate of 25 Mt) is orders of magnitude higher than that consumed by mineral reactions (Gilfillan et al., 2009), leaving the overall isotopic composition of the gas intact. We also assume that the isotopic fractionation caused by the potential CO₂ dissolution in formation water would cause an insignificant effect from fractionation compared to the degree of overlap observed here (Gilfillan et al., 2009).

In summary, the isotope analysis on dawsonite suggests magmatic origin for the majority of the CO₂ from which the dawsonite crystallized. (Fig. 4). In contrast, the calculated $\delta^{13}\text{C}_{\text{CO}_2}$ values in equilibrium with siderite and ultimately the source of the CO₂ from where siderite precipitated from is not obvious. The genesis of these carbonates is more complex. Based on the measured carbon isotope composition of siderite, two groups can be distinguished: Group-1 (heavy): from +4.2‰ to

+4.3‰ and Group-2 (light): from +1.3‰ to +2.1‰ (Table 2).

In the Group-1 samples, the calculated $\delta^{13}\text{C}_{\text{CO}_2}$ values in equilibrium with siderite (−6.0‰ - −3.9‰; Table 3) fall closer to the calculated values from dawsonites and to the European SCLM (Fig. 4). It means that siderite may also have precipitated as an effect of CO₂ flooding in the study area. The inter-mixed petrographic feature of dawsonite and siderite (Fig. 2D) might support this scenario.

However, in case of Group-2, the calculated $\delta^{13}\text{C}_{\text{CO}_2}$ values (−8.4‰ - −6.1‰; Table 3) are significantly lighter than those calculated from dawsonites and lighter than that observed in the free CO₂ gas (Fig. 4). These findings indicate that: 1) the CO₂ present during the precipitation of siderite belonging to Group-2, has a different origin. This is difficult to envisage in light of the consistency of the dawsonite data, along with the conclusions on a single CO₂ source in the Mihályi-Répcelak field (Palcsu et al., 2014; Vető et al., 2014); 2) the CO₂ present during the precipitation of siderite belonging to Group-2, did not have a different origin but it went through some degree of fractionation by dissolution into water, relative to its isotopic composition when Group-1 was formed (along with dawsonite). This could imply that siderite belonging to Group-2 represents a different age group than Group-1. Although dating siderite is beyond the scope of this work, we think that this may be a reasonable explanation considering the variety of its fabric features (see Section 4.1); and 3) as not all the siderite shows close textural relations to dawsonite, at least some part of the siderite could have formed before CO₂ flooding, likely representing an early diagenetic mineral rather than a product of CO₂ flooding. These observations reinforce that stable carbon isotopes provide an excellent tool to distinguish diagenetic carbonates from CO₂ flooding-related mineral precipitations and/or the timing of formation in the Mihályi-Répcelak field.

Dawsonite formation associated by CO₂ flooding in a geological system has been found in several basins worldwide (Table S1). The plot of the calculated $\delta^{13}\text{C}_{\text{CO}_2}$ values in equilibrium with dawsonite (Fig. 4) shows that most of the data related to CO₂ reservoirs overlap with the mantle/magmatic derived carbon sources (from −8‰ to −4‰; Ohmoto and Rye, 1979). In contrast, the stable isotope composition of dawsonite found in hydrothermal mineral deposits in Albania (Ferrini et al., 2003) show a distinct isotope signature (Koman area in Fig. 5) and the calculated $\delta^{13}\text{C}_{\text{CO}_2}$ values in equilibrium with the Albanian dawsonite plot away from this magmatic range characterized by a well-separated isotope signature (Fig. 4; from −0.1‰ to +1.2‰). Data from reservoirs worldwide form a positive linear trend (Fig. 5), except for the samples from East China Basin (Zhao et al., 2018). Our data from the Mihályi-Répcelak field fit well into this trend. This positive trend and the observed wider range in oxygen isotopic composition of the whole compiled dataset (Fig. 5) is likely linked to sensitivity of the oxygen isotope composition to the local porewater and CO₂ compositions together. This highly variable composition of oxygen isotope highlights to the significance of the local conditions and processes that took place during the CO₂ flooding and dawsonite formation.

5.3. Origin of the porewater

Dawsonite in theory provides an exceptional opportunity to determine the origin of porewater during CO₂ flooding as, besides oxygen, it contains hydrogen within the structural OH[−], of which isotopic composition must be strongly related to the porewater. However, it has not yet been exploited as all studies to date focused only on the carbon and oxygen isotope determinations (Baker et al., 1995; Comerio et al., 2014; Ferrini et al., 2003; Gao et al., 2009; Golab et al., 2006; Li and Li, 2017; Liu et al., 2011; Ming et al., 2017; Uysal et al., 2011; Zhao et al., 2018; Zhou et al., 2014). However, our present interpretation is based on our new measurements of both oxygen and hydrogen isotopic ratios of dawsonites. As the hydrogen isotope fractionation factor is not known for the dawsonite-water system, a fractionation factor of another OH-bearing mineral needs to be utilised. Based on experiments (Chesworth, 1971) and natural samples (e.g. Goldbery and Loughnan, 1977),

Table 3

Calculated $\delta^{13}\text{C}_{\text{CO}_2}$ in a binary CO₂ - dawsonite and CO₂ - siderite equilibrium at two different temperatures.

Area	Sample	$\delta^{13}\text{C}_{\text{CO}_2}$ [‰, PDB]		References
		T = 70 °C	T = 98 °C	
	RM6-9R	−3.9	−2.0	Bottinga (1986)
	Dawsonite-1	−4.5	−2.6	Ohmoto and Rye (1979)
Mihályi	RM6-9R	−4.0	−2.0	Bottinga (1986)
	Dawsonite-2	−4.5	−2.6	Ohmoto and Rye (1979)
	RM6-9R Siderite-1	−8.2	−6.1	Golyshev et al. (1981)
	RM6-9R Siderite-2	−8.4	−6.3	
	RM6-7R3 Siderite	−6.0	−3.9	
		RM6-7R1 Siderite	−6.0	−4.0
	RM32-5R2	−4.2	−2.2	Bottinga (1986)
Répcelak	Dawsonite	−4.8	−2.8	Ohmoto and Rye (1979)
	RM19-6R Siderite	−8.9	−6.8	Golyshev et al. (1981)

Calculations used carbonate-CO₂ fractionation equation (Bottinga, 1968; Golyshev et al., 1981; Ohmoto and Rye, 1979) see Eq. S1-S3 in Suppl.

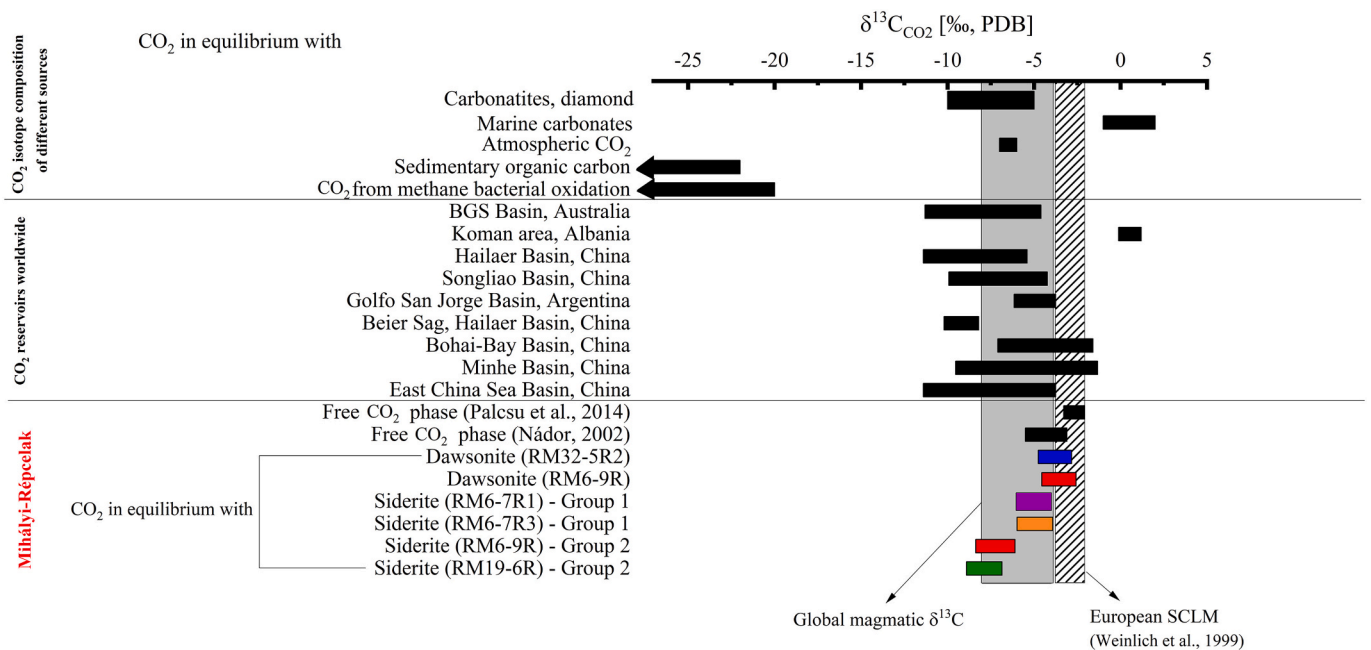


Fig. 4. Calculated $\delta^{13}\text{C}_{\text{CO}_2}$ in equilibrium with separated dawsonite and siderite along with carbon isotope ranges of free CO_2 fluid from Mihályi-Répcelak compared to that of a selection of carbonate reservoirs worldwide. Our CO_2 data calculated from measured dawsonite isotopic compositions (blue and red rectangles) overlaps with that of locally determined free CO_2 fluid and proposed European SCLM compositions. Thus, we suggest that dawsonite was formed from the magmatic CO_2 . Calculated $\delta^{13}\text{C}_{\text{CO}_2}$ in equilibrium with siderite forms two groups: Group-1 falls close to the European SCLM composition suggesting that one part of siderite formed as a response to CO_2 flooding event (Fig. 2D), Group-2 indicates that CO_2 which was present during the formation of large ($\sim 200 \mu\text{m}$) siderite patches either altered from its original composition by fractionation or this group of siderite is unrelated to CO_2 inflow (Fig. 2B). Literature data are from: Baker et al., 1995; Comerio et al., 2014; Craig, 1953; Ferrini et al., 2003; Gao et al., 2009; Golab et al., 2006; Hoefs, 1997; Li and Li, 2017; Liu et al., 2011; Ming et al., 2017; Ohmoto and Rye, 1979; Schidlowski, 2001; Uysal et al., 2011; Zhao et al., 2018; Zhou et al., 2014. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

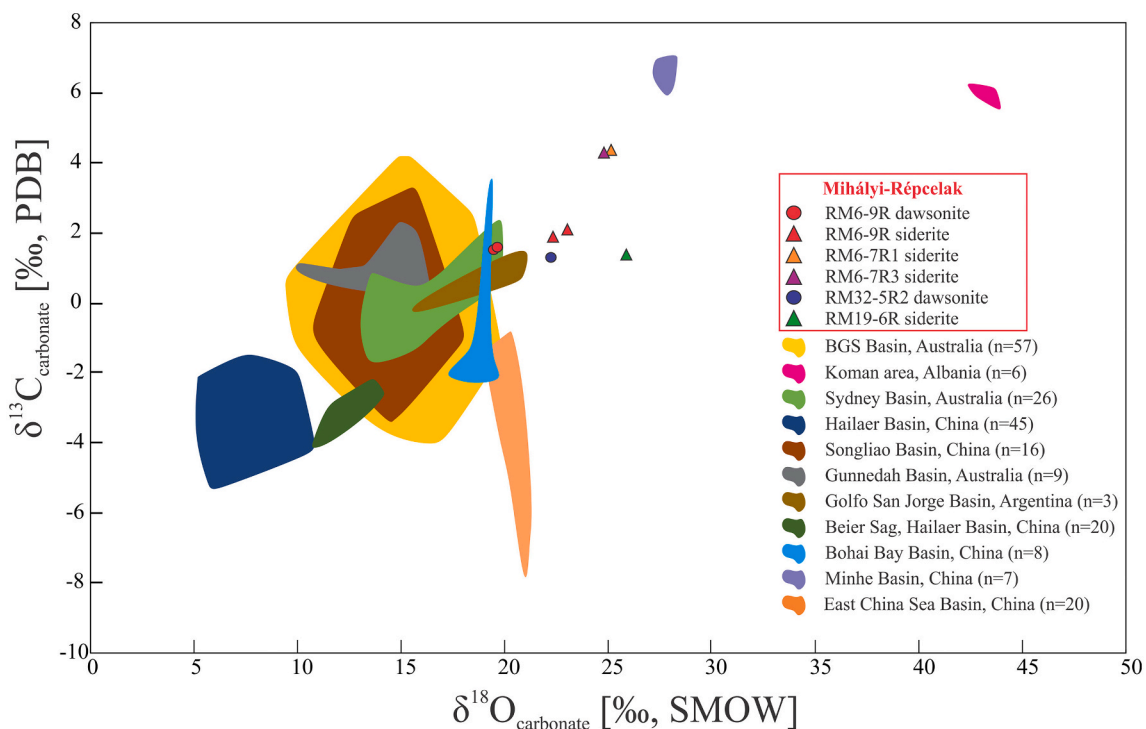


Fig. 5. Stable C and O isotope composition of dawsonite-bearing sandstones from the Mihályi-Répcelak (circles) area compared with dawsonite-bearing rocks from other studies. Our data fits into the generally observed positive correlation. This suggests the observed wide range in oxygen isotopic composition is likely linked to sensitivity of the oxygen isotope composition to the local porewater and CO_2 compositions together and draws attention to the significance of the local conditions and processes that took place during the CO_2 flooding and dawsonite formation. 'n' is the number of data. Relevant data are from Baker et al., 1995; Comerio et al., 2014; Ferrini et al., 2003; Gao et al., 2009; Golab et al., 2006; Li and Li, 2017; Liu et al., 2011; Ming et al., 2017; Uysal et al., 2011; Zhao et al., 2018; Zhou et al., 2014.

the polymorph of $\text{Al}(\text{OH})_3$ (gibbsite, bayerite, nordstrandite; Chesworth, 1971) or boehmite [$\text{AlO}(\text{OH})$] can form in a geological reservoir similar to the one presented in this study, which grants further investigation into these candidates. It has been found that at $T < 51$ °C gibbsite incorporates the lighter hydrogen isotope during its formation (Chen et al., 1988; Vitali et al., 2001). Since the OH^- in the dawsonite is also connected to Al octahedrons (Łodziana et al., 2011) we suggest that H isotopic fractionation in the gibbsite – H_2O system is similar to dawsonite – H_2O systems. Therefore, we calculated the hydrogen isotope composition of porewater in equilibrium with dawsonite using the gibbsite- H_2O fractionation equation (Méheut et al., 2010; Eq. S4 in Suppl.) (Table 4).

The measured δD values of the studied dawsonite scatter around $-60 \pm 2\text{‰}$, except RM6-9R sample, which is characterized by value of -74‰ (see Section 4.3). The calculated $\delta\text{D}_{\text{H}_2\text{O}}$ values are between -86‰ and -91‰ at 70 °C and -69‰ – -74‰ at 98 °C for the RM6-7R1, RM6-7R2, RM6-7R3, RM32-5R2, RM19-6R, and for RM6-9R are -103‰ at 70 °C and -86‰ at 98 °C (Table 4).

To determine the oxygen isotope composition of porewater in equilibrium with dawsonite, we used the calcite-water fractionation factor (O'Neil et al., 1969; Eq. S5) at temperatures of 70 °C and 98 °C. The calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values for RM6-9R ranges from -1.4‰ to $+2.1\text{‰}$, whereas the calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values in dawsonite from the RM32-5R2 range between $+1.3\text{‰}$ and $+4.7\text{‰}$ (Table 5).

The calculated $\delta\text{D}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values in equilibrium with RM6-9R and RM32-5R2, and available groundwater data (Bükkfürdő; Nádor, 2002) are presented in the δD - $\delta^{18}\text{O}$ diagram (Fig. 6). The calculated isotope values are plotting on the right side of the Global Meteoric Water Line (GMWL; Craig, 1961). Assuming that the original fluid has a meteoric origin (falls on the GMWL) the observed systematics (i.e. enrichment in ^{18}O) can be caused by interaction with country rock with an elevated oxygen isotope composition. Generally, the carbonate, metamorphic and magmatic rocks are characterized by $\delta^{18}\text{O}$ values above 2‰ (Clark et al., 1997), thus this shift in the data relative to GMWL indicates enhanced modification of the isotopic ratios of the porewater due to (CO_2 -)water-rock interactions (Clark et al., 1997).

As the data plot close to the global magmatic field, some contribution from a magmatic source (Taylor, 1974) can be envisioned as well. This possibility can especially be realistic because it was found that the majority of the CO_2 that triggered the dawsonite formation, also has a magmatic origin. However, the contribution of the magma-originated water is likely subordinate compared to the groundwater circulating in the basin (Tóth et al., 2016).

5.4. Applications to mineral storage of carbon-dioxide and future directions

Recent advances in engineered mineral storage of carbon-dioxide have been seen in basaltic and ultramafic rocks (Goldberg et al., 2018; Marieni et al., 2021; Matter et al., 2016; Pogge von Strandmann et al., 2019; Snæbjörnsdóttir et al., 2017; Snæbjörnsdóttir et al., 2020). Formation of calcite and dolomite has been traced in small scales by

Table 4

Estimated δD values of porewater from the dawsonite-bearing sandstone samples calculated with gibbsite- H_2O fractionation factor (Eq. S4 in Suppl., Méheut et al., 2010).

Area	Sample	$\delta\text{D}_{\text{H}_2\text{O}}$ [‰, SMOW]	
		T = 70 °C	T = 98 °C
Mihályi	RM6-9R	-103	-86
	RM6-7R3	-89	-72
	RM6-7R2	-88	-71
	RM6-7R1	-90	-73
	RM32-5R2	-86	-69
Répcelak	RM19-6R	-91	-74

Table 5

Calculated oxygen isotope composition of porewater ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) in equilibrium with dawsonite at two different temperatures in the Mihályi-Répcelak field.

Area	Sample	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ [‰, SMOW]	
		T = 70 °C	T = 98 °C
Mihályi	RM6-9R Dawsonite-1	-1.4	+2.1
	RM6-9R Dawsonite-2	-1.4	+2.0
Répcelak	RM32-5R2 Dawsonite	+1.3	+4.7

Calculation used calcite-water fractionation equation (O'Neil et al., 1969) see Eq. S5 in Suppl.

carbonate recovery and Ca-isotope geochemistry (Pogge von Strandmann et al., 2019). Although these works have been crucial in our advanced understanding of mineral storage of carbon-dioxide, large-scale experiments remain little explored, which lifts a barrier in the implementation of industrial mineral storage of carbon-dioxide. Although natural CO_2 reservoirs provide opportunities to study CO_2 mineralization in large scales (Gilfillan et al., 2009; Güleç and Hilton, 2016; Zhou et al., 2012), these reservoirs also highlight on the increasing need to focus on more complex carbonate systems because natural sandstone reservoirs always contain complex carbonate assemblages. Geochemical modelling studies also indicate the existence of this assemblage complexity both in CO_2 injection projects and natural systems (e.g., De Silva et al., 2015; Király et al., 2016a; Xu et al., 2003).

To increase our understanding in real CO_2 storage scenarios, it is necessary that more complex, multi-carbonate systems are studied in real CO_2 injection experiments. In this study we have identified the origin of multiple carbonate minerals and distinguished different generations using stable isotope geochemistry. Based on these results, some of the carbonates (e.g., dawsonite) almost certainly formed as a response to large-scale CO_2 flooding in the Mihályi-Répcelak natural CO_2 reservoir. We can now estimate the total amount of trapped CO_2 in dawsonite. Considering a reasonable average concentration of dawsonite in one of the dawsonite-bearing reservoirs (~ 3.5 w/w %) and an average reservoir rock density of 2.4 g/cm³, we can calculate that ~ 25.5 kg CO_2 has been trapped in 1 m³ reservoir rock (Table 6). This agrees with results from Király et al. (2017) (20 kg CO_2 /m³ rock), obtained from geochemical modelling. Based on our samples, the RM19-6R reservoir, which is the biggest reservoir in this study, trapped the highest amount of CO_2 (8.18×10^5 t) in dawsonite alone (Table 6). Now an average total reservoir volume is 8.24×10^7 m³, we calculate the total CO_2 trapped as dawsonite to be 2.01×10^6 t (Table 6), larger than quantified ever before. Although this degree of mineralization may not seem to be significant from large-scale CO_2 storage point of view, it shows that thermodynamic conditions are given for significant mineralization and it certainly sparks the following 'what if' question: What if the well-known phenomenon of decreasing reservoir pressure changes the reservoir conditions (pH, cation supply) (Hellevang et al., 2005; Liu et al., 2019; Raistrick et al., 2009; Watson et al., 2004) occurs along a gradient that would result in a net increase in carbonate minerals? The Mihályi-Répcelak field has seen decades is removal of CO_2 at the level of ~ 100 kt/year for commercial reasons (Mészáros et al., 1979). Would this place the Mihályi-Répcelak field into the position of providing a unique opportunity to study mineral storage of carbon and how to 'tune' a field for that?

In future CO_2 injection studies, we suggest that the different carbonates (e.g. calcite, dolomite, ankerite, dawsonite and siderite) identified in the reservoir should be separated and geochemically studied (e.g. isotope analysis) to allow deconvoluting of carbonation processes. This can possibly help to constrain better the conditions and processes that take place in the reservoir and provide background information for secure mineral storage of carbon-dioxide in the reservoir.

The extension of the classic carbon and oxygen isotope analysis of dawsonite by the addition of hydrogen isotope determinations has opened a door to the simultaneous determinations of the origin of both

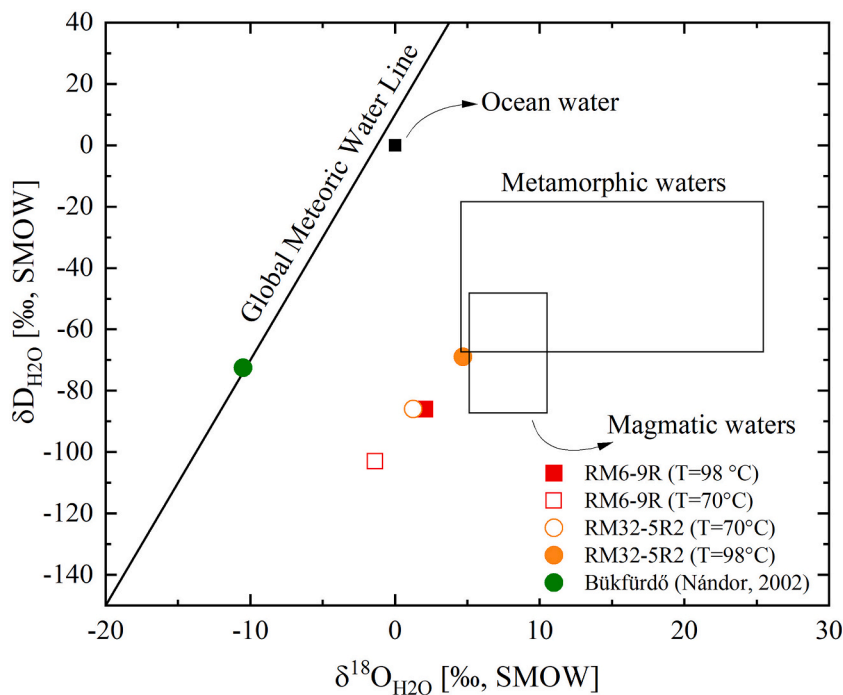


Fig. 6. Estimated porewater δD and $\delta^{18}O$ values in equilibrium with samples RM6-9R (red square) and RM32-5R2 (orange square). Our data show a shift compared to the Global Meteoric Water Line, which could indicate an enhanced modification of the isotopic ratios of the porewater likely due to the CO_2 -water-rock interactions. The estimated data plot close to the global magmatic water field, some contribution from magmatic source can be envisioned as well. However, the contribution of the magma-originated water is likely subordinate compared to the groundwater circulating in the basin. Groundwater data from the vicinity (i.e., Bükfürdő; green circle) of the studied location and ranges of major water types. Magmatic and metamorphic values are from Taylor, (1974). Modified after Brownlow (1996), Rice (1993), Shepard (1986). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 6

Determined volume of trapped CO_2 in dawsonite mineral.

Area	Sample	Rock volume for the whole reservoir [m^3]	Mineral trapping for 1 m^3 rock [t/m^3]	Mineral trapping for the whole reservoir [t]
Mihályi	RM6-7R1, 7R2, 7R3	$2.87 \cdot 10^7$	$2.45 \cdot 10^{-2}$	$7.02 \cdot 10^5$
Répcelak	RM32-5R2, RM32-5R1	$1.65 \cdot 10^7$	$3.00 \cdot 10^{-2}$	$4.87 \cdot 10^5$
	RM19-6R	$3.72 \cdot 10^7$	$2.20 \cdot 10^{-2}$	$8.18 \cdot 10^5$
		sum: $8.24 \cdot 10^7$	average: $2.55 \cdot 10^{-2}$	sum: $2.01 \cdot 10^6$

Reservoir volumes are from Mészáros et al. (1979).

RM32-5R1 does not contain dawsonite.

The amount of CO_2 trapped in the reservoir was calculated based on the following: The mass of dawsonite was calculated from the modal abundance of dawsonite in the reservoir rock (~ 3.5 w/w % on average) multiplied with the assumed density of the reservoir rock ($2400 \text{ kg}/m^3$). By dividing the mass of with the molar mass of dawsonite ($143.9 \text{ kg}/\text{kmol}$) we can calculate the molar amount of the mineral, which equals with the molar amount of the trapped CO_2 (since 1 mol CO_2 can trap 1 mol dawsonite according to the following equation: $albite + CO_2 + H_2O \rightarrow dawsonite + 3 \text{ quartz}$). Thus, the mass of CO_2 can be calculated by multiplying its molar amount with the molar mass of CO_2 ($44.01 \text{ kg}/\text{kmol}$).

the CO_2 and pore water, which dawsonite formed from. Should dawsonite be found to be more common with regards to CO_2 injections, this new technique will help to constrain the processes, which play a crucial role in the fluid (gas-liquid)-rock system and to monitor the injected CO_2 during geological CO_2 storage.

6. Conclusion

We studied the stable isotope composition of carbonates in a natural CO_2 occurrence in the Mihályi-Répcelak field. We separated dawsonite and siderite from other carbonates and from each other for C and O isotope analyses. The CO_2 that precipitated as dawsonite seems to be magmatic in origin having also similar isotopic composition to that of European SCLM. Thus, we suggest that dawsonite precipitation is related to magmatic CO_2 'injection' in the Mihályi-Répcelak field. In contrast, the same isotopic signature comparison suggests that part of the siderite formed as a response to CO_2 flooding, the rest being either early diagenetic that formed before the CO_2 flooding or precipitated from a fractionated magmatic CO_2 . The additional δD analyses of the OH^- group of dawsonite a powerful isotope geochemical tool is developed that can trace origin of the porewater and gas-water-rock interactions more precisely than before. This combined technique may be employed in the future to effectively trace in-reservoir fluid rock

interactions on the field and provide inevitable input data for future geochemical modelling works and move mineral CO_2 storage forward.

Author Contribution

Conceptualization of the project: Gy.F., Sample collection: Gy.F., D. Cs., Cs.K., Sample preparation: D.Cs., Cs.K., V.F., Cs.Sz., Gy.F., Laboratory analysis: D.Cs., Gy.Cz., Cs.K., Cs.Sz., Gy.F., I.K., Data interpretation: D.Cs., Gy.Cz., Cs.K., Cs.Sz., Gy.F., A.D., D.Gy., Writing—original draft preparation: D.Cs., Gy.Cz., Gy.F., D.Gy., Cs.K., Writing and Editing: Cs. Sz., A.D., V.F.

All authors have read and agreed to the published version of the manuscript.

Declaration of Competing Interest

The Authors declare no conflict of interest.

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Appendix A. Supplementary data

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