

IR spectroscopy as a fast method of determining carbonate content in the Sarmatian–Badenian sandstone reservoirs: A case study from the Carpathian Foredeep (Poland)

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Abstract: The work describes and compares the methods for determination of the carbonate content in fifteen samples of Sarmatian–Badenian sandstones, which are reservoir rocks for natural gas in the central part of the Carpathian Foredeep in Poland. Typical sandstone samples were taken from a depth of 1600–2000 m.b.s. (*metres below the surface*) from drilling cores from well W-1 located about 4 km south of Sędziszów Małopolski, for the development and testing of a new technique for determining the carbonate content. Sandstones are composed of mainly quartz (up to 82 %), then carbonates (calcite and dolomite), feldspar, micas, rarely glauconite and pyrite. The carbonate content of reservoirs is very important for making decisions regarding to intensification of gas production by acid treatment of a near-wellbore region of sandstone. The carbonate content in the tested samples was determined using Scheibler's volumetric method, petrographic modal data and ATR FT-IR spectroscopy (*Attenuated Total Reflectance Fourier Transformation-Infrared Spectroscopy*). According to the volumetric and petrographic analyses, the average carbonate content in the tested sandstones was 14.57 and 20.50 vol. %. The similar value 14.51 % (standard deviation in comparison to other methodologies is 0.59–7.75 %) has been obtained by simple and fast ATR FT-IR spectroscopy based on integration of the band coming from out-of-plane bending vibration of the CO₃²⁻ group (ν_2) about 870 cm⁻¹. A comparison of obtained data showed that the ATR FT-IR procedure has the potential to be routinely used for determination of the carbonate content in sandstone samples.

Keywords: carbonate, Miocene sandstone, reservoir rock, natural gas, ATR FT-IR method.

Introduction

According to Szuflicki et al. (2020), in the area of the Carpathian Foredeep there are 108 natural gas reservoirs, of which 85 were being exploited up to 2019. Many reservoirs are drilled in Miocene sandstones, although there are some new Miocene reservoirs with a low depletion rate. For many of these nearly depleted deposits, the use of intensification methods is necessary to prolong extraction at an economically viable level.

According to Walker et al. (1991) and Jewulski (2007), the most common well-stimulation techniques are acid treatment and hydraulic fracturing. Acid treatment is one of the oldest methods of production intensification used for over 100 years. However, there are still some restrictions and requirements associated with this method, particularly in the case of sandstones with carbonate cements. The acid treatment of such rocks is complicated due to multiple stages of process and fluid reactions with minerals in the host rock. In recent years, many useful articles have been published concerning the acidization of sandstone that could be helpful in the design of acid treatment processes in clastic rock formations. The innovations concerned optimizing the composition of the acidic agent, (usually a mixture of HCl and HF) for

specific reservoir conditions (McLeod et al. 1983; Li et al. 2015; Shafiq et al. 2016; Shafiq & Mahmud 2017; Leong & Mahmud 2019). Preliminary laboratory tests of reservoir rocks are an important step in choosing an adequate intensification method. McLeod's guidelines for sandstone acidizing (McLeod 1984) describe the influence of acid treatment on rock reservoir mineralogy. Recently, many reports described the results of successful acidizing of the mineral compositions in the sandstone reservoirs. The percentage of quartz, feldspar, clay, chlorite, and silt in the rock should be taken into account for appropriate acidification method (Simon & Anderson 1990; Chiu et al. 1993; Coulter & Jennings 1999; McLeod & Norman 2000). Another important issue is the carbonate content of the rock. Generally, sandstones contain more than 15–20 % carbonates but the acidizing treatment of a near wellbore zone may be performed only by hydrochloric acid (Kalfayan & Metcalf 2001; Kalfayan 2008; Shafiq & Mahmud 2017). In such cases, the application of HF is not necessary and stimulation with acid proceeds similarly to that in a carbonate reservoir (Kalfayan & Metcalf 2001; Kalfayan 2008; Shafiq & Mahmud 2017).

The quantitative determination of the carbonate content in sediments is carried out using various techniques, the most

popular of which are XRD (*X-ray diffraction*) (Hardy & Tucker 1988; Bish & Post 1989), TA (*thermal analysis*) (Labus 2017) and volumetric analysis (Knödel et al. 2007). Petrographic analysis is used as one of the basic techniques for describing rocks, for example, to determine mineral composition and carbonate content (Folk 1980; Hickey et al. 2007; Pettijohn et al. 2012).

Infrared spectroscopy has also been used successfully to determine the carbonate content in such samples. For example, Bosch Reig et al. (2002) proposed FT-IR (*Fourier Transform Infrared Spectroscopy*) quantitative analysis for the measurement of calcium carbonate content from KBr pellets using potassium ferricyanide as the standard. Udvardi et al. (2014) demonstrated that the ATR FT-IR method could be complementary to the classic TA and XRD methods in classifying natural sediments. For the purposes of quantitative analysis, the integration of bands coming from carbonates in the ranges of $1235\text{--}1585\text{ cm}^{-1}$ and $874\pm 2\text{ cm}^{-1}$ was used (Udvardi et al. 2014). Müller et al. (2014) proposed a methodology for classifying and quantifying various mineral components (also calcite and dolomite) in shale rock samples using ATR FT-IR spectroscopy. Bruckman & Wriessing (2013) showed that a combination of FT-IR spectroscopy and X-ray diffraction is useful for modelling based on partial least squares regression to measure the carbonate content in soil. Mroczkowska-Szerszeń & Orzechowski (2018) showed that FT-IR ATR spectroscopy analysis (based on use of statistical methods like PCR (*Principal Component Regression*) or PLS (*Partial Least Squares*)) allows quantitative and semi-quantitative screening analysis of reservoir rock samples. Stanienda-Pilecki (2019) showed that FT-IR spectroscopy is a suitable method for identification of carbonate phases differing in magnesium content from the Triassic limestone samples.

The aim of the work is assessment of optimization of carbonate analyses in the sediments. The first step of this work is to determine the carbonate content in Sarmatian–Badenian sandstone samples, which are common gas-bearing reservoir rocks in the area of the Carpathian Foredeep in Poland. The carbonate content is determined using the volumetric method (Scheibler's method) and petrographic study. These data obtained may be helpful in assessing the possibility of using intensifying production methods in gas-producing wells from the Miocene sandstones of the Carpathian Foredeep. The second step is to investigate the quality of using ATR FT-IR spectroscopy for determination of carbonate content in the same type of sample.

Geological setting

The early to middle Miocene Carpathian Foredeep, the Polish eastern part of which is shown in Fig. 1, is a part of a large sedimentary basin developed as a peripheral foreland basin related to the moving Carpathian front. In the west, the Carpathian Foredeep is linked to the Alpine Molasse Basin, and in

the east, it passes into the Balkan foreland basin (Oszczypko et al. 2006). The basin is filled with predominantly clastic sediments of the Miocene age at the Carpathian front in Poland and Ukraine (Kotarba 2012).

The Polish Carpathian Foredeep consists of three structural complexes: 1) Precambrian–Paleozoic–Mesozoic basement, 2) folded Zgólbice and Stebnik units (inner foredeep; Lower to Middle Miocene deposits), and 3) autochthonous Miocene sediments (outer foredeep; flat-lying Middle Miocene marine deposits). The eastern part of the outer Carpathian Foredeep Basin between Kraków and the Ukrainian state border (Fig. 1) is filled with Badenian and Lower Sarmatian, mostly sandy–clayey sediments up to 4500 m in total thickness (Kotarba 2012). These sediments are underlain by the basement of the European Platform, covered mainly by Permian–Mesozoic terrestrial and shelf sediments and locally by Paleogene deposits (Oszczypko et al. 2006, and references therein).

The Paleozoic, Mesozoic and Tertiary strata of the Carpathian Foredeep are oil and gas productive. The main source rocks of the Paleozoic and Mesozoic basement which generated mainly thermogenic and microbial gas and to a lesser extent also oil, are siliciclastic and carbonate rocks of Ordovician, Silurian, Devonian, Lower Carboniferous and Middle Jurassic age (e.g., Karnkowski 1999; Kotarba 2012; Roubal et al. 2020). The major reservoir rocks in the Paleozoic–Mesozoic basement are Middle and Upper Devonian carbonates, Lower Carboniferous carbonates, Triassic sandstones, Malm limestones, Cenomanian and Upper Cretaceous sandstones. The traps in oil and gas deposits of the Paleozoic–Mesozoic basement are sealed both by the Miocene and Upper Cretaceous marls and in some cases by the Carpathian Overthrust and flysch strata (Kotarba & Jawor 1993; Karnkowski 1999; Florek et al. 2006; Myśliwiec et al. 2006).

Hydrocarbon accumulations of mostly gas, gas-condensate and locally oil occur in the Miocene sediments (e.g., Karnkowski 1999; Kotarba 2011; Kotarba et al. 2011). Several sedimentary environments containing sandstones with hydrocarbon accumulations have been identified. From the bottom up, there are turbidite sandstones of submarine fans, delta sediments, and shallow-sea sediments of estuaries, sandy barriers and lagoons (Oszczypko 1996; Olszewska 1999; Myśliwiec 2004a; Krzywiec 2006; Oszczypko et al. 2006). The main reservoir rocks are Lower Badenian glauconitic sandstones, Middle Badenian evaporites, and Upper Badenian–Lower Sarmatian sandstones deposited in submarine fan, deltaic and shallow marine environments (Myśliwiec et al. 2006).

The average porosity of the sandstone reservoirs, analysed from drill cores, varies from 9 to 35 % and the permeability ranges from ca 200 mD up to 900 mD (Karnkowski 1999; Myśliwiec 2004a; Myśliwiec et al. 2006). The major types of traps in the Miocene of the Carpathian Foredeep are: a) compactional anticlines situated above basement uplifts, b) traps sealed by the Carpathian Overthrust plane, c) traps sealed by faults, d) stratigraphic pinch-out traps, and, e) stratigraphic traps related to unconformities.

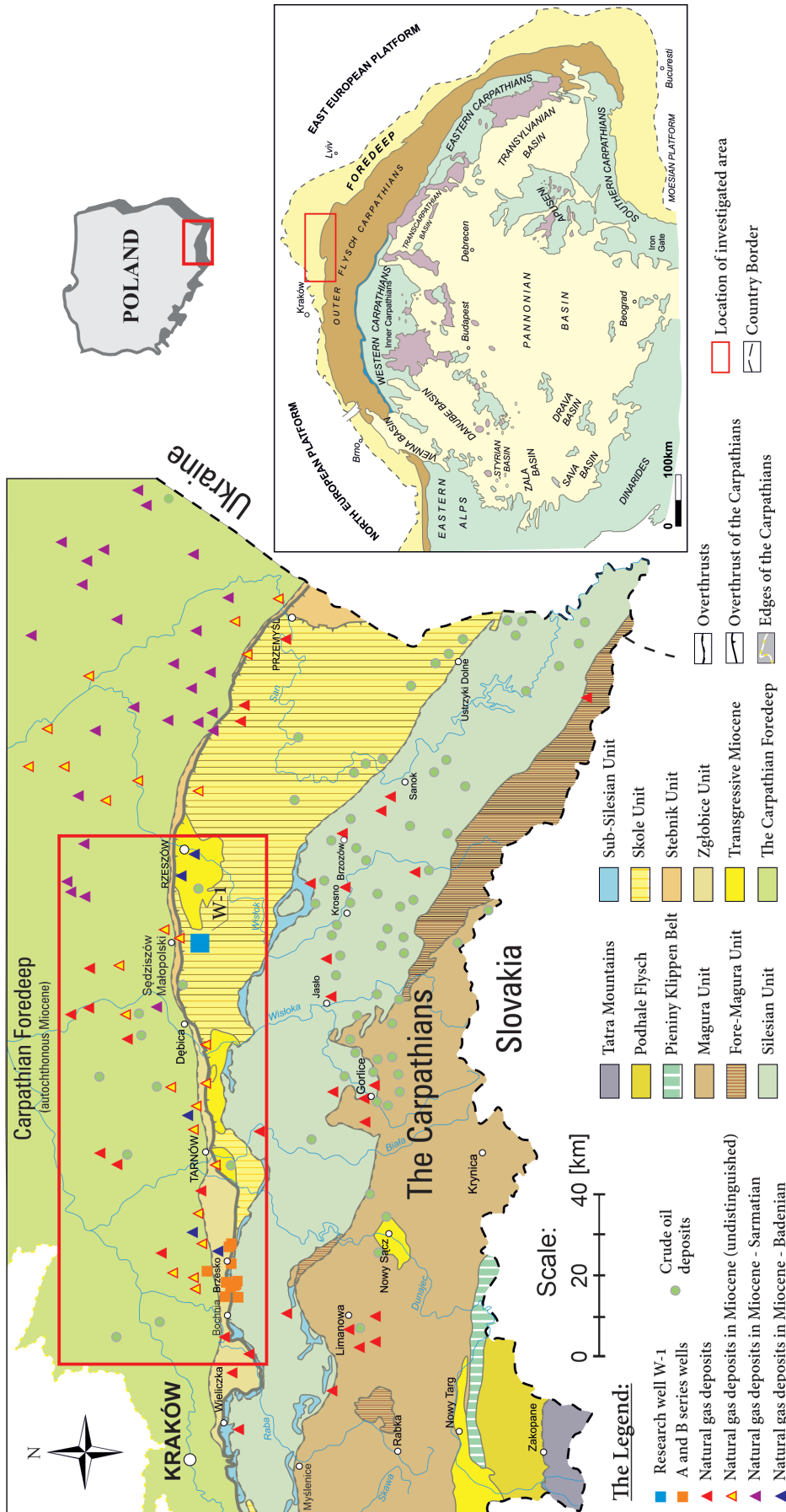


Fig. 1. A simplified geological map of the Outer Carpathians and their foreland between Kraków and the Ukrainian state border. Location of the study area, studied well W-1, location of A and B well series (Hollendorfer 1995) and distribution of hydrocarbon deposits are shown. Modified from Kováč et al. 1998; Kamkowski 1999; Mysliwiec 2004a,b; Krobicki & Golonka 2008; Lis & Wysocka 2012; Golonka et al. 2018; Szufiicki et al. 2020.

The Carpathian Foredeep belongs to the largest petroleum province in Central Europe. Hydrocarbon resources (*ca.* 2.72×10^5 tons of oil and 1.092×10^{12} m³ of natural gas) have been explored and extracted for decades (Szuflicki et al. 2020). Many of the fields are currently at the mature stage (Karnkowski 1999; Myśliwiec et al. 2006).

In the research area, the Zgólbice Unit has been thrust over the Middle Miocene Carpathian Foredeep sediments. It is represented by strongly disturbed and folded Miocene deposits. The unit is built of gritty shales interbedded with sandstones, gypsum, anhydrites and siltstones. The total thickness of the strata differs due to the shape of the formation and ranges from several dozen to 1000 m (Olszewska et al. 2007).

The Skole Unit, which in this region determines the maximum northern range of the Carpathians, is shifted to the Zgólbice Unit. The Skole Unit forms a series of slices moving southwards, within which are numerous synclines, anticlines and folds displaced by transverse strike-slip faults. The oldest flysch deposits include shales, sandstones, fucoid marls, conglomerates and shales of the Lower and Upper Cretaceous. Their thicknesses range from a few to several metres. Paleogene flysch formations are Eocene mottled slates and hieroglyphic layers, and Oligocene Menilite shales. The thicknesses of individual layers vary from a few tens to several hundred metres (Olszewska et al. 2007).

Folded and eroded strata of Skole Unit are partially covered by parautochthonous (transgressive) Miocene sediments (sandstones, limestones, claystones, siltstones) not exceeding 200 m in thickness (Marciniak & Zimnal 1999).

Research well W-1 (Fig. 1.) is located about 4 km south of Sędziszów Małopolski town. The drilling cores used in our studies are taken from the depth from 1600 to 2000 m.b.s., from three gas-bearing horizons. Lithologically, there are fine-grained sandstones (see chapter “Analysis of scanned images of thin sections of the investigated sandstone”) of Badenian–Sarmatian age (undistinguished).

Methodology

Samples

Fifteen samples of Sarmatian–Badenian sandstones from reservoir rocks from the central part of the Carpathian Foredeep in Poland were chosen from the collection of drilling cores belonging to the Department of Petroleum Engineering, Faculty of Drilling, Oil and Gas, AGH University of Science and Technology in Kraków. Each drill core sample had diameters of 10×15 cm.

Petrographic analysis

The petrographic analysis of sandstone was performed by optical transilluminated light microscopy. Fifteen thin sections that had been polished with chromium (III) oxide were studied

with a Carl Zeiss AxioVision transmission microscope. The quantitative analysis of the samples was performed in accordance with the recommendations of Ratajczak et al. (1998). A point counting method was used with an ELTINOR 4 integration table and image analysis based on ImageJ software. The measurements consisted in the identification and registration of grains, appearing in turn on the measuring line of a grid. At least 300-point counts were performed in each thin section, at intervals selected depending on the grain size.

ATR FT-IR spectral analysis

ATR FT-IR spectra of the samples were recorded using FT-IR spectrometer (Nicolet™ IR200 spectrometer, Thermo Fisher Scientific, Waltham, MA, USA) equipped with a diamond ATR accessory, a DTGS KBr detector, and a KBr beam splitter. To provide good repeatability and reproducibility of the measurements, the samples were ground in a grinder and sieved. Finally, after these processes the particle size was up to 200 μm. The spectra were collected at room temperature in the mid-infrared spectral range (4000–400 cm⁻¹) with a spectral resolution of 2 cm⁻¹. The background spectrum was collected before each measurement; 32 scans were collected during each measurement.

The sample was poured onto the diamond window of the ATR accessory to form a small cone that covered the window completely. The pressure clamp was then screwed into the cone of the sample so it was pressed on the diamond window. The spectra of each sandstone sample were averaged from 3 raw spectra with no manipulation or post-processing. The average variation was *ca.* 0.003.

Measurements of mixtures of pure calcite and quartz (Merck, Germany) were used to build a calibration curve for the quantitative determination of the carbonate content in the samples. The prepared mixtures included 5, 7, 10, 12, 15, 17, 20, 22 and 25 mass percent of calcite. The spectra were averaged from six raw spectra; no manipulation or post-processing was used.

Carbonate content determination using Scheibler's method

The carbonate content in 15 sandstones was determined using Scheibler's method, which is a classic volumetric method that is used to determine the carbonate content in soil by international standards (ISO 10693: 1995, Soil quality, Determination of carbonate content – volumetric method). Therefore, Scheibler's method is often used as a reference method.

About 20 g of each drilling core was finely ground for the measurements using Scheibler's method. The samples (1 g of each) were mixed with 15 % HCl for 15 minutes and the volumes of evolving CO₂ were measured. All the measurements were repeated three times. Equation (1) was used to calculate the carbonate content in mass %:

$$y = \frac{V \cdot K}{m} \quad (1)$$

where:

V – volume of released CO₂ [cm³] (accuracy: 0.1 ml);
 m – mass of the sample [g] (accuracy: 0.01 g); K=f(p,t) – coefficient that depends on temperature and pressure (K= 0.39504 for p=734 mmHg and t=21 °C).

Results and discussion

Analysis of scanned images of thin sections of the investigated sandstone

The matrix of the sandstones is formed by small- to medium-grained (0.05–0.50 mm) quartz monocrystalline and polycrystalline particles (Fig. 2), which is the main component of grain framework. Feldspars (albite) and micas (muscovite) can also be observed with rare glauconite and pyrite. Generally, it is a loosely packed and well-sorted deposition with some thin low-porosity zones. The roundness of the grains ranges from angular to subrounded, but generally subangular (Pettijohn et al. 2012; Ulmer-Scholle et al. 2014; MacKenzie

et al. 2017). Some quartz particles appear darker because of iron minerals. Cementation can be described as an inconsistent contact-clod type. The sandstones are cemented by a combination of quartz overgrowth in the form of a grain shell and precipitated cements of calcite/dolomite and clay minerals. The matrix is composed of clay minerals and iron hydroxides. Fragments of sedimentary rocks (limestones) and igneous rocks (granitoids) are occasionally observed. The Miocene sandstones in the eastern part of Carpathian Foredeep (Poland), Kozłowska et al. (2011) identified by SEM (*scanning electron microscope*) investigations contain subordinate ankerite and siderite. Carbonate foraminifera bioclasts are present as well. The calculated modal compositions of the sandstone samples from the grain counting are presented in Table 1.

The results of the petrographic analyses presented in this study (the series C) and the results reported in the study by Hollendonner (1995), who analysed autochthonous Miocene sandstones in the western part of the Polish Carpathian Foredeep (Fig. 1, well series A and B), are shown in the Quartz–Feldspar–Carbonate ternary diagram for comparison (Fig. 3). The diagram shows some differences between the individual

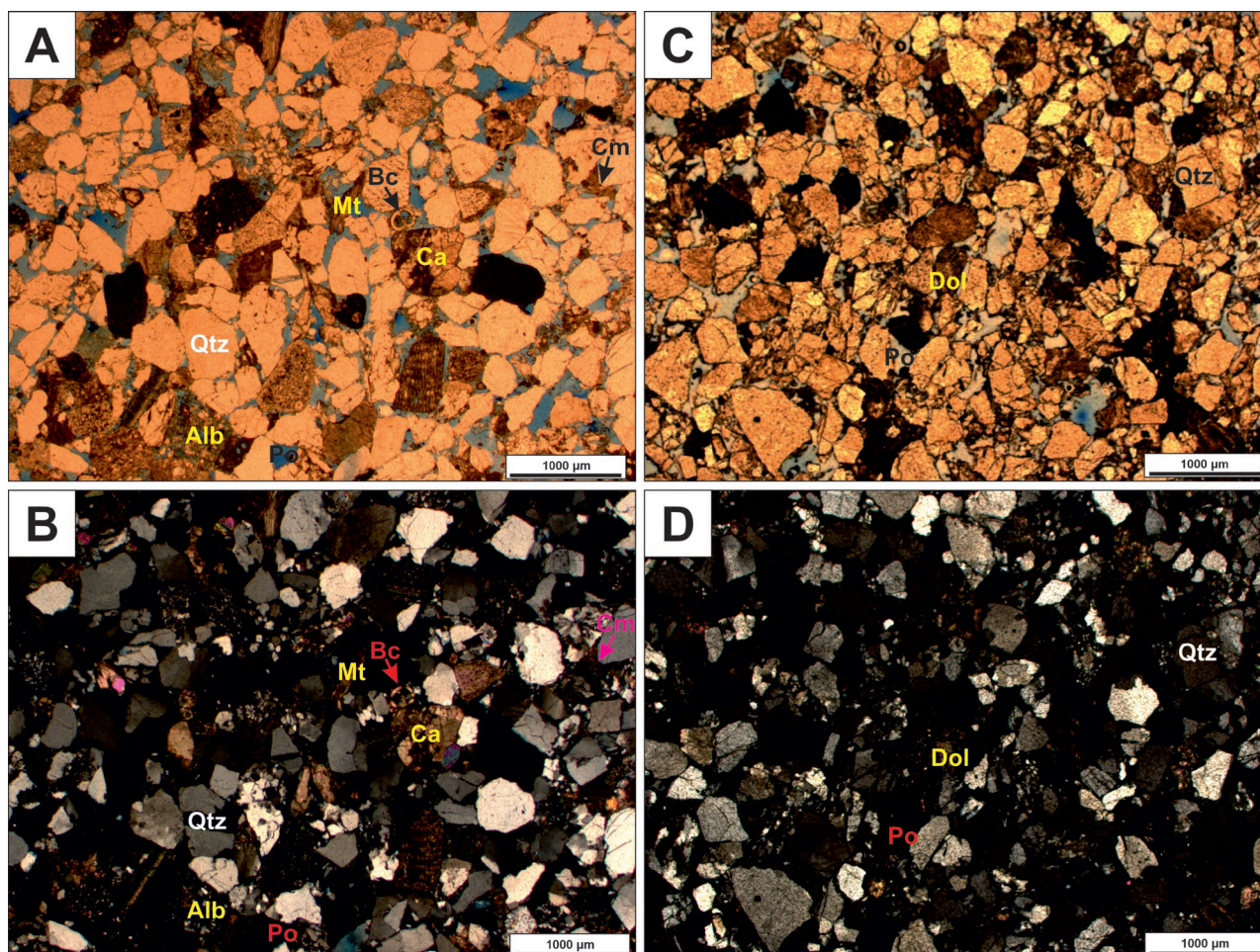


Fig. 2. Photomicrographs from the thin sections of a sandstone impregnated with blue epoxy; A, C — parallel nicols; B, D — crossed nicols; Qtz – quartz, Bc – bioclast, Ca – calcite, Dol – dolomite, Alb – albite, Cm – carbonate cement, Mt – muscovite, Po – pore.

Table 1: Compositions of the sandstone samples, calculated from the results of grain counting.

Sample	Depth [m]	Stratigraphy	Lithology	Quartz [%]	Feldspar (albite) [%]	Mica (muscovite) [%]	Carbonates (calcite+dolomite) [%]	Matrix [%]	Others [%]
1	1624.55	Sarmatian–Badenian	sandstone	64.00	4.92	7.69	19.08	2.15	2.15
2	1626.40	Sarmatian–Badenian	sandstone	61.76	3.27	9.80	21.57	1.96	1.63
3	1627.70	Sarmatian–Badenian	sandstone	62.19	11.56	0.00	21.25	3.75	1.25
4	1628.35	Sarmatian–Badenian	sandstone	73.00	0.40	0.40	26.20	0.00	0.00
5	1629.65	Sarmatian–Badenian	sandstone	59.16	6.43	2.89	28.94	1.93	0.64
6	1848.75	Sarmatian–Badenian	sandstone	60.26	10.60	3.97	20.53	2.32	2.32
7	1849.80	Sarmatian–Badenian	sandstone	63.64	5.84	2.60	22.73	2.27	2.92
8	1850.20	Sarmatian–Badenian	sandstone	73.78	1.50	4.12	20.60	0.00	0.00
9	1852.00	Sarmatian–Badenian	sandstone	82.44	0.38	0.76	15.65	0.00	0.76
10	1855.10	Sarmatian–Badenian	sandstone	63.31	6.82	0.97	26.95	1.62	0.32
11	1856.55	Sarmatian–Badenian	sandstone	61.84	2.96	2.30	20.07	11.18	1.64
12	1985.65	Sarmatian–Badenian	sandstone	76.70	2.91	2.59	14.24	0.00	3.56
13	1986.80	Sarmatian–Badenian	sandstone	66.45	9.21	2.63	17.11	2.30	2.30
14	1988.25	Sarmatian–Badenian	sandstone	71.35	6.51	3.65	17.45	0.00	1.04
15	1993.25	Sarmatian–Badenian	sandstone	77.42	3.23	0.65	15.16	0.97	2.58

sample sets in terms of carbonate content in the sandstones. Sandstones from the western part of the Carpathian Foredeep (series A and B) contain 3 to 20 vol. % of carbonates, and the sandstones from the central part (the series C) up to 30 vol. %. Other studies also mention the content of carbonates in the Carpathian Foredeep. According to Ratajczak & Szafran (1982) and Myśliwiec (2004a), Sarmatian sandstones from the eastern part of the Carpathian Foredeep contain up to 20 % of carbonates, especially detrital limestone mud.

ATR FT-IR spectroscopy analysis

The ATR FT-IR spectra of the investigated sandstone samples in the range 4000–400 cm^{-1} are presented in Figure 4. The spectral 4000–1800 cm^{-1} range mainly contains the absorption bands from CO_2 vibration (at 2340 cm^{-1}). In a few samples, a weak band at 3610 cm^{-1} was observed, which can be assigned to the –OH group vibration that originates from clay minerals and micas (Vaculíková & Plevová 2005; Du et al. 2010; Müller et al. 2014; Madejova et al. 2017).

The most prominent bands in the spectra of the sandstone samples are the result of absorption of quartz, which is obvious because according to the petrographic analysis the content of the quartz ranges from 59.16 vol. % to 82.44 vol. % (see Fig. 3, Table 1). The strongest bands are observed at *ca.* 1000 cm^{-1} (maximum of the band at *ca.* 1000 cm^{-1} , in fact a broad band in the range of 1200–900 cm^{-1}) and 455 cm^{-1} , which can be assigned to the asymmetric stretching vibration of the Si–O group and the asymmetric Si–O bending mode, respectively. Medium-intensity bands can be seen at 795 and 775 cm^{-1} . They are the result of the symmetrical stretch of the Si–O bond. In the spectra, the symmetrical Si–O bending modes are observed as bands at 690 and 515 cm^{-1} (medium-intensity bands) (Saikia et al. 2008). However, it is worth emphasizing that some of the quartz absorption bands overlap with bands originating from muscovite (the high intensity bands in the spectrum of muscovite are at 1026 cm^{-1} and

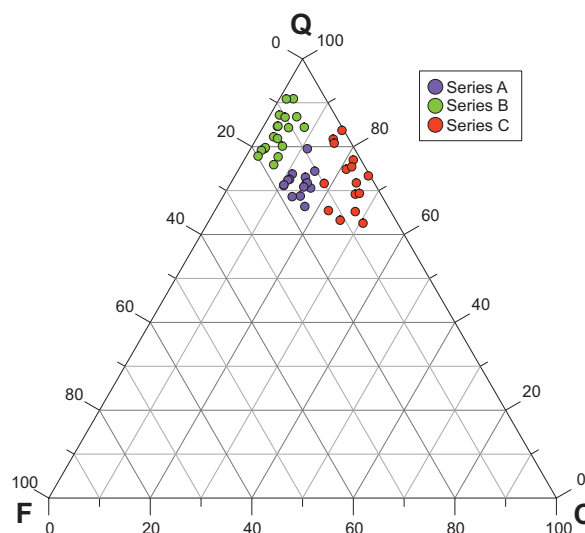


Fig. 3. Ternary diagram of the content of quartz, feldspar and carbonates (vol. %) in the Miocene sandstones of the Polish Carpathian Foredeep, which shows the results of petrographic analyses by Hollendonner (1995) (series A and B) and the current study (series C). The sandstones from series A, B and C were taken from depths of 500–700 m, 800–1000 m, and 1600–2000 m.b.s., respectively.

474 cm^{-1}), feldspar (the most prominent band at 1034 cm^{-1}), and clay minerals (the high-intensity bands in the spectrum of illite are at 1024 cm^{-1} and 471 cm^{-1} ; the high-intensity bands in the spectrum of kaolinite are at 1032 cm^{-1} , 538 cm^{-1} and 1039 cm^{-1} ; the high-intensity bands in the spectrum of montmorillonite are at 522 cm^{-1} and 466 cm^{-1}) (Vaculíková & Plevová 2005; Du et al. 2010; Madejová et al. 2017).

The second-largest component of the tested sandstone samples is carbonate minerals, which are visible in the spectrum as bands originating from carbonate ion CO_3^{2-} . The most significant absorption bands in the spectra of the carbonates are seen at *ca.* 1400 cm^{-1} (the most intense band, which

originates from the symmetrical stretch of the CO_3^{2-} group, ν_3) and about 870 cm^{-1} (the out-of-plane bending vibration of the CO_3^{2-} group, ν_2) (Chester & Elderfield 1967). The characteristic major absorption peaks of the CO_3^{2-} ion are slightly shifted in various carbonate minerals. The position of appropriate bands are mainly dependent on crystal structure and the atomic radius or mass of the cations contained in the isomorphous groups. For example, the spectra of calcite and dolomite (carbonates which are very common in this type of rock sample) differ from each other in terms of the location of the band resulting from the in-plane bending vibration of CO_3^{2-} group (ν_4), so that the absorption is shifted from 710 cm^{-1} (calcite) to 725 cm^{-1} (dolomite). In the spectra of the investigated sandstone samples, absorption bands at $\sim 710\text{ cm}^{-1}$ and at 725 cm^{-1} could be seen, indicating that the tested samples contained both calcite and dolomite. As mentioned in the introduction, infrared spectroscopy may be useful for determining the carbonate content of geological samples (Bosch Reig et al. 2002; Müller et al. 2014; Udvardi et al. 2014). In this study, the IR spectroscopy is applied for semi-quantitative analysis of carbonate content in the examined sandstone samples, therefore we chose the band around 870 cm^{-1} . As can be seen in Figure 5, the band ca. 870 cm^{-1} , which is caused by the out-of-plane bending vibration of CO_3^{2-} group (ν_2), may be successfully used to determine the carbonate content of sandstone samples. The known carbonate minerals like: calcite, dolomite, siderite, magnesite, ankerite, rhodochrosite, smithsonite, kutnahorite, aragonite, strontianite and witherite have absorption of ν_2 bands in the range of $890\text{--}850\text{ cm}^{-1}$ (Huang & Kerr 1960). This band was selected for quantitative analysis because neither quartz nor feldspar (albite and orthoclase) show infrared absorption in this spectral range (Müller et al. 2014). In this spectral range, no intense bands are observed in the IR spectra of other sample components, such as mica and clay minerals (Vaculíková & Plevová 2005; Du et al. 2010).

Figure 6 shows a good linear dependence between the integration of the band around 870 cm^{-1} in the range $890\text{--}850\text{ cm}^{-1}$ and the content of calcite in the artificial samples (mixtures of calcite and quartz with the calcite content (m/m): 5, 7, 10, 12, 15, 17, 20, 22 and 25 %), ($R=0.995$, $R^2=0.990$, standard deviation 0.028).

The calibration curve presented in Figure 6 was applied to calculate the carbonate content in the investigated sandstone samples. The results of the calculations using the infrared spectroscopy method are shown in Table 2.

Volumetric calciminer method – Scheibler's method

Calcimetry is a laboratory technique for providing rapid and reliable measurements of the amount of carbonates in samples from cores, cuttings and soils (Ettensohn 2018). Carbonates

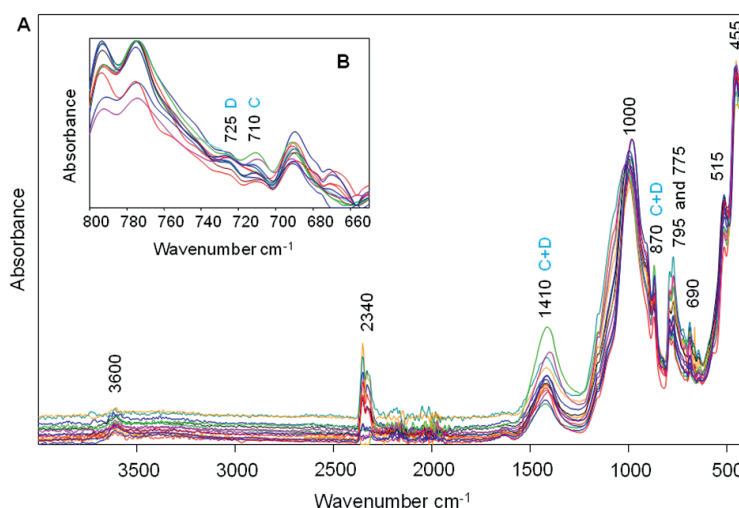


Fig. 4. ATR FT-IR spectra of the investigated sandstone samples: A — in the range $4000\text{--}400\text{ cm}^{-1}$; B — in the range $800\text{--}650\text{ cm}^{-1}$. C – calcite, D – dolomite.

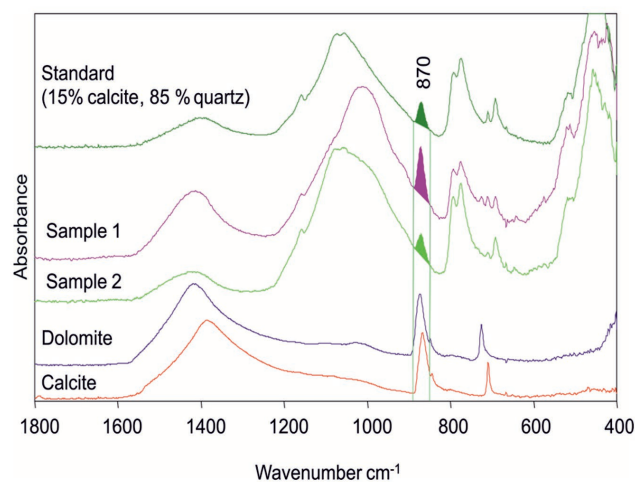
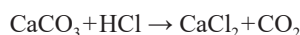


Fig. 5. ATR FT-IR spectra for: calcite, dolomite, 2 randomly selected sandstone samples, and a sample of the standard mixtures (mixture of powdered calcite and quartz, 15 % calcite m/m).

can be measured by dissolving a sample in hydrochloric acid solution and then determining either acid consumption or appropriate salt or CO_2 production.

An example reaction equation for calcite is shown below:



In fact, the reaction rate of various carbonate minerals with HCl is different (Ettensohn 2018). For calcite and aragonite this reaction is rapid at room conditions. Dolomite decomposes slowly and requires a longer reaction time. On the other hand, cold acid reaction with siderite and magnesite is very weak.

In this work, the carbonate content in the tested samples was examined indirectly by measuring the volume of emitted CO_2 . Taking into account the experimental conditions (room temperature, atmospheric pressure), the measurements

determined the content of calcite and partially dolomite in the tested samples. The results obtained by volumetric method were shown in Table 2.

Comparison of content carbonate determined by the volumetric method (Scheibler's method), petrographic study, and ATR FT-IR spectroscopy

Comparison of carbonate content determined by different methods are presented in Tables 2 and 3. The results from IR spectroscopy and the data obtained by Scheibler's method are shown in Table 2. In both methods, samples prepared in the same way were tested (powdered and sieved sandstone sample). Additionally, Table 2 shows the results of the petrographic analysis. It should be mentioned that only a small

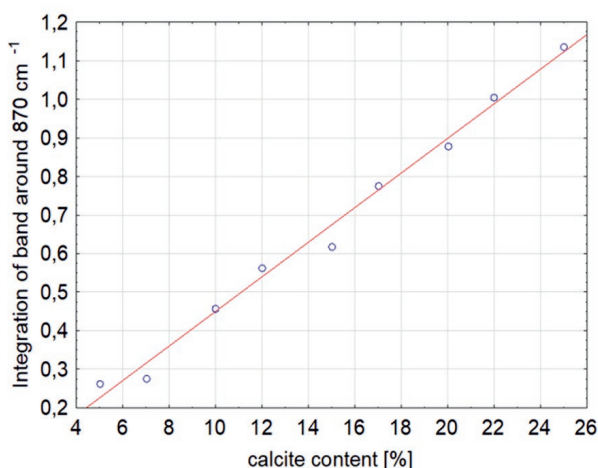


Fig. 6. Calibration curve (dependence of the relative integration of the band at 870 cm^{-1} versus the mass percentage of calcite in the sample).

Table 2: The carbonate content of the studied sandstone samples measured by the volumetric method (Scheibler's method), petrographic study, and ATR FT-IR spectroscopy.

Sample	Depth [m]	Carbonate content in the sandstone samples			
		Scheibler's method [%]	Petrographic analysis [%]	ATR FT-IR method [%]	Standard deviation [%]
1	1624.55	19.75	19.08	23.00	2.10
2	1626.40	19.36	21.57	20.58	1.11
3	1627.70	16.59	21.25	17.41	2.49
4	1628.35	14.22	26.20	13.74	7.06
5	1629.65	19.75	28.94	18.15	5.82
6	1848.75	18.67	20.53	16.99	1.77
7	1849.80	13.04	22.73	10.31	6.53
8	1850.20	13.83	20.60	11.78	4.62
9	1852.00	15.41	15.65	16.53	0.59
10	1855.10	14.02	26.95	13.07	7.75
11	1856.55	12.35	20.07	12.09	4.53
12	1985.65	9.48	14.24	8.93	2.92
13	1986.80	11.46	17.11	11.49	3.25
14	1988.25	9.88	17.45	12.38	3.86
15	1993.25	10.86	15.16	11.18	2.40

selected fragment of the core was examined by the petrographic method.

The various analytical methods used in this work show the ability to detect carbonate minerals (petrography method – calcite and dolomite, volumetric method – calcite and partially dolomite, and the method of infrared spectroscopy – the whole group of carbonate minerals). However, the ATR FT-IR spectroscopy method and Scheibler's method give similar results because tested sandstone samples have been prepared in the same way. The carbonate content obtained by ATR FT-IR spectroscopy and the results from Scheibler's method are in good agreement ($R=0.91$, $R^2=0.83$, standard deviation 1.50) (see Fig. 7).

Most of the previously proposed applications of IR spectroscopy with the use of KBr pellets require much more time for sample preparation. The ATR technique has so far been rarely used for these purposes (Müller et al. 2014; Udvardi et al. 2014). Udvardi et al. (2014) showed that the ATR FT-IR method could be complementary to the classic TA and XRD methods in classifying natural sediments. They quantitatively analysed two bands from carbonates ($1235\text{--}1585\text{ cm}^{-1}$ and $874\pm 2\text{ cm}^{-1}$). Müller et al. (2014) proposed a complicated methodology for quantifying different mineral components (also calcite and dolomite) present in shale rock samples that involved a combination of ATR-IR spectroscopy and a multivariate regression model based on partial least squares (PLS). The advantage of the proposed ATR FT-IR procedure is that it is a simple and fast method for determining the carbonate content in sandstones, as it is based exclusively on the integration of the band from out-of-plane bending vibration of the CO_3^{2-} group (ν_2) at 870 cm^{-1} in the $890\text{--}850\text{ cm}^{-1}$ range.

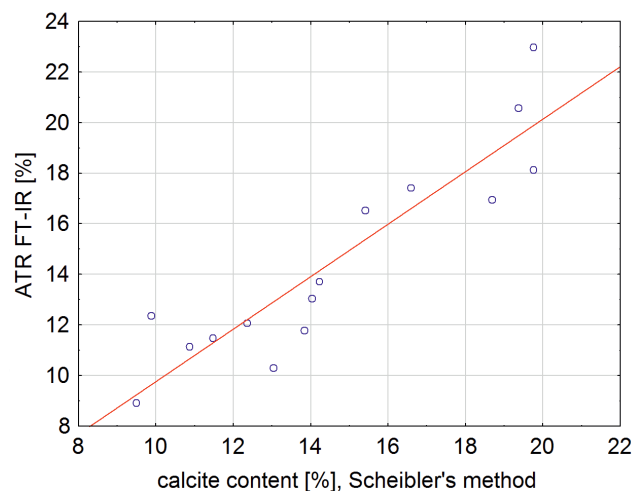
Compared to other carbonate determination methods, ATR FT-IR spectroscopy has some advantages: as it does not require special preparation compared to petrographic analysis (that need thin sections), and, unlike Scheibler's method, which use chemicals. ATR FT-IR spectroscopy is a rapid method, and portable, high-quality spectrometers are commercially available that allow an analysis of test samples under field conditions.

In general, the results of measurement of the carbonate minerals content obtained by all the tested methods are in good agreement and the average values are 14.57, 14.51 and 20.50 % for the volumetric, spectroscopic and petrographic methods, respectively (Table 3).

The highest carbonate content was observed by the petrographic method but a reliable comparison with the other methods is difficult. The difference is not only in the identification of the content of different minerals because in the case of IR spectroscopy and the volumetric method, the signal comes from a volumetrically significant averaged composition, but the petrographic method covers only a small area of the core sample.

Table 3: The carbonate content of the tested sandstone samples. Basic statistical data.

Method	Average [%]	Median [%]	Minimum value [%]	Maximum value [%]	Standard deviation
Volumetric	14.57	14.02	9.48	19.75	3.56
Spectroscopic	14.51	13.07	8.93	23.00	4.06
Petrographic	20.50	20.53	14.24	28.94	4.36

**Fig. 7.** The correlation of the carbonate content for 15 natural samples, obtained by Scheibler's method versus IR spectroscopy.

Conclusions

The carbonate content was analysed in a set of fifteen samples of Badenian–Sarmatian reservoir sandstones located in the depth of 1600–2000 m.b.s. in the Polish central part of the Carpathian Foredeep. Samples were taken from drill cores from well W-1 situated about 4 km south of Sędziszów Małopolski. Three different methods – volumetric, spectroscopic and petrographic were used to assess the carbonate content. The average carbonate content in the sandstones was determined to be 14.6 vol. % (by volumetric method), 14.5 vol. % (by ATR FT-IR spectroscopic method) and 20.5 vol. % (by petrographic method).

The study proved that the application of ATR FT-IR spectroscopy is a reliable, simple, fast, and effective method for the determination of carbonate content in reservoir sandstones. This new technique is exclusively based on interpretation of the band from out-of-plane bending vibration of the CO_3^{2-} group (ν_2) at about 870 cm^{-1} in the $890\text{--}850\text{ cm}^{-1}$ range. ATR FT-IR spectroscopy has a potential to be routinely used as it provides results comparable to those given by other methods.

Mineralogy of sandstone reservoirs is one of the main parameters influencing the modern design of production-intensification programs or procedures concerning the acid treatment of near-wellbore zones. Above all, knowledge of the carbonate content in rocks is very important. Reliable determination of the carbonate content can help us to decide

on the use of hydrochloric acid instead of a mixture of hydrochloric acid and hydrofluoric acid, which is of great importance not only in terms of effective intensification of hydrocarbon extraction, but also from an ecological point of view.

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