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Reservoir quality and petrophysical properties of Cambrian sandstones and their changes during the experimental modelling of CO_2 storage in the Baltic Basin

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Abstract. The objectives of this study were (1) to review current recommendations on storage reservoirs and classify their quality using experimental data of sandstones of the Deimena Formation of Cambrian Series 3, (2) to determine how the possible CO_2 geological storage (CGS) in the Deimena Formation sandstones affects their properties and reservoir quality and (3) to apply the proposed classification to the storage reservoirs and their changes during CGS in the Baltic Basin.

The new classification of the reservoir quality of rocks for CGS in terms of gas permeability and porosity was proposed for the sandstones of the Deimena Formation covered by Lower Ordovician clayey and carbonate cap rocks in the Baltic sedimentary basin. Based on permeability the sandstones were divided into four groups showing their practical usability for CGS (‘very appropriate’, ‘appropriate’, ‘cautionary’ and ‘not appropriate’). According to porosity, eight reservoir quality classes were distinguished within these groups.

The petrophysical, geochemical and mineralogical parameters of the sandstones from the onshore South Kandava and offshore E6 structures in Latvia and the E7 structure in Lithuania were studied before and after the CO_2 injection-like alteration experiment. The greatest changes in the composition and properties were determined in the carbonate-cemented sandstones from the uppermost part of the South Kandava onshore structure. Partial dissolution of pore-filling carbonate cement (ankerite and calcite) and displacement of clay cement blocking pores caused significant increase in the effective porosity of the samples, drastic increase in their permeability and decrease in grain and bulk density, P- and S-wave velocity, and weight of the dry samples. As a result of these alterations, carbonate-cemented sandstones of initially ‘very low’ reservoir quality (class VIII), ‘not appropriate’ for CGS, acquired an ‘appropriate’ for CGS ‘moderate’ quality (class IV) or ‘very appropriate’ ‘high-2’ reservoir quality (class II). The permeability of the clay-cemented sandstones of ‘very low’ reservoir quality class VIII from the lower part of the E7 reservoir was not improved. Only minor changes during the alteration experiment in the offshore pure quartz sandstones from the E6 and E7 structures caused slight variations in their properties. The initial reservoir quality of these sandstones (‘high-1’ and ‘good’, classes I and III, respectively, in the E6 structure, and ‘cautionary-2’, class VI in the E7 structure) was mainly preserved.

The reservoir sandstones of the Deimena Formation in the South Kandava structure had an average porosity of 21%, identical to the porosity of rocks in the E6 structure, but twice higher average permeability, 300 and 150 mD, respectively. The estimated good reservoir quality of these sandstones was assessed as ‘appropriate’ for CGS. The reservoir quality of the sandstones from the E7 offshore structure, estimated as ‘cautionary-2’ (average porosity 12% and permeability 40 mD), was lowest among the studied structures and was assessed as ‘cautionary’ for CGS.

Petrophysical alteration of sandstones induced by laboratory-simulated CGS was studied for the first time in the Baltic Basin. The obtained results are important for understanding the physical processes that may occur during CO_2 storage in the Baltic onshore and offshore structures.

Key words: CO_2 geological storage, Deimena Formation, porosity, permeability, reservoir quality, rock properties, Baltic Basin, offshore structure.

INTRODUCTION

The reduction of the greenhouse effect of the Earth’s atmosphere is a major concern for researchers and everyone who cares about the future of our planet. This research is related to one of the most promising technologies and fields of study, which is considered to be an effective measure for mitigating the climate change induced by greenhouse gases (Metz et al. 2005; Bachu et al. 2007; Arts et al. 2008; IPCC 2014). The scientific community agrees on the importance of reducing industrial carbon dioxide (CO_2) emissions in the atmosphere using CO_2 Capture and Geological Storage (CCS) in, for example, (1) deep saline aquifers, (2) depleted oil and gas fields, (3) unmineable coal seams and (4) porous basalt formations. The global economic potential of CCS would amount to 220–2200 Gt of CO_2 cumulatively, which would mean that CCS contributes 15–55% of the total mitigation effort worldwide until 2100, averaged over a range of baseline scenarios (Metz et al. 2005). Worldwide, a number of known pilot storage and large-scale CCS demonstration projects are ongoing and/or monitored, the first of which, Sleipner (Norway), started in 1996. Nevertheless, there are gaps in the knowledge of short- and long-term (10–100 and 100–10 000 years, respectively) phenomena accompanying the process of the storage of CO_2 in deep geological formations.

Our study concentrates on CO_2 storage in deep saline aquifers (>800 m depth, >35 g L^{-1} salinity), composed of reservoir rocks overlain by the cap rock (seal). This is the most widespread worldwide option currently under consideration for CO_2 Geological Storage (CGS). The sandstones of the Deimena Formation of Cambrian Series 3 (earlier Middle Cambrian; Sundberg et al. 2011; Peng et al. 2012) in the Baltic Basin are characterized by highly variable porosity and permeability, which are not considered in the available classifications of reservoir rocks and recommendations on CO_2 storage reservoirs.

The current research aims at the assessment of the quality of reservoir rocks for CGS based on the properties of reservoir quartz sandstones and their changes caused by acidic fluid during experimentally modelled CGS. Because mineralogical and petrophysical alterations are usually site-specific, this study is important for gaining parameters for the petrophysical modelling of the CO_2 plume to predict the CO_2 fate in short and long term, and to demonstrate the effectiveness of the geophysical monitoring of the storage site before, during and after the CO_2 injection in the Baltic sedimentary basin.

The objectives of this study were (1) to review the available recommendations on storage reservoirs and offer a classification of their quality using experimental data of the Deimena Formation sandstones of Cambrian Series 3, (2) to determine the influence of possible CGS in the sandstones of the Deimena Formation on their properties and reservoir quality and (3) to apply the proposed classification to the storage reservoirs and their evolution during CGS in the Baltic Basin.

The obtained data will be used in 4D time-lapse numerical seismic modelling to support more reliable petrophysical and geophysical models of the CO_2 plume.

GEOLOGICAL BACKGROUND

The main target for the CGS study in Estonia, Latvia and Lithuania is the Baltic Basin (700 km × 500 km synclinal structure), a Late Ediacaran–Phanerozoic polygenetic sedimentary basin that developed in a pericratonic setting in the western part of the East European Platform. It overlies the Palaeoproterozoic crystalline basement of the East European Craton, specifically the West Lithuanian Granulite Domain, flanked by terranes of the Svecofennian Orogen southeast of the Baltic Sea (Gorbatschev & Bogdanova 1993). Basin fill consists of Ediacaran–Lower Palaeozoic, Devonian–Carboniferous and Permian–Mesozoic successions, coinciding with what are referred to as the Caledonian, Variscan and Alpine stages of the tectonic development of the basin, respectively. These are separated by regional unconformities and overlain by a thin cover of Cenozoic deposits (Poprawa et al. 1999). The Cambrian Series 3 saline aquifer (depth 650–1700 m), located in the central-western part of the Baltic Basin, suits best for the CO_2 storage in the Baltic Region. It is composed of 25–80 m thick Deimena Formation sandstone, covered by up to 46 m thick shales and clayey carbonate primary cap rocks of the Lower Ordovician Zebre Formation. Shale rocks are dark, thin-layered (0.5–2 mm) and highly fissile. A 0.5 m layer of greenish-grey glauconite-bearing sandy marlstones with minor limestone lenses is observed at the base of the onshore Zebre Formation. The reservoir rocks are also covered by 130–230 m thick Ordovician and 100–225 m thick Silurian impermeable clayey carbonate secondary cap rocks. Clayey rocks can be easily determined by increased values of gamma-ray readings in all the studied wells, and they play an essential role as a seal for the studied structures (Fig. 1).

The regional theoretical storage potential of Cambrian sandstone saline aquifers below 800 m in the Baltic Sea Region has been estimated as 16 Gt (Vernon et al. 2013). The average storage capacity of the Cambrian reservoir is 145 Mt in the western part of the Baltic Basin in the S41/Dalders structure of the Swedish offshore sector, while the average capacity of the regional Cambrian Faludden trap is 5.58 Gt (Sopher et al. 2014). For comparison, the total estimated storage capacity in the Jurassic sandstone formations in the Norwegian Sea is 5.5 Gt (Halland et al. 2013). The Utsira sandstone formation at the first storage site in the world, Sleipner in the North Sea, has a storage capacity of approximately 15 Gt (Halland et al. 2011).

The Cambrian aquifer includes potable water in the northern shallow part of the Baltic Basin, mineral water (salinity 10 g L^{-1}) in southern Estonia and saline water in the Deimena Formation at more than 800 m depths, with salinity up to 120 g L^{-1} in the central and 150–180 g L^{-1} in the southern and western parts of the basin, where fluid temperature reaches 88 °C (Zdanavičiute & Sakalauskas 2001). The last mentioned geochemical and pressure–temperature conditions of formation fluids allow the use of the Deimena Formation reservoir for

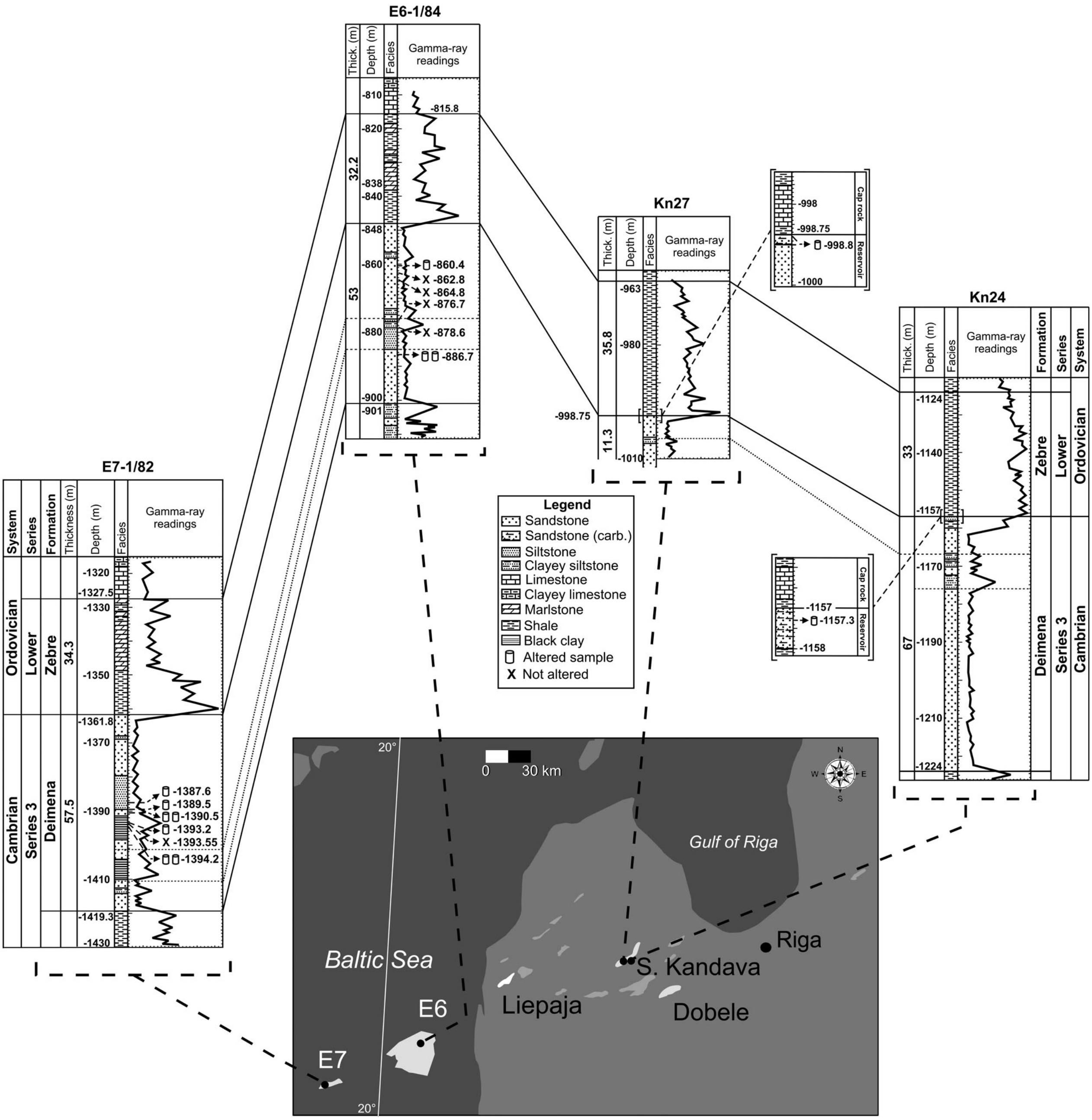

Fig. 1. Correlation of boreholes from the studied offshore E6 and E7 structures (E6-1/84 and E7-1/82) and onshore South Kandava (S. Kandava, Kn24, Kn27) focusing on the sandstone reservoir of the Deimena Formation of Cambrian Series 3. Cap rocks are represented by the Lower Ordovician Zebre Formation (primary cap rock) and part of the secondary cap rock (Middle Ordovician Kriukai Formation). Gamma-ray readings were digitized from analogous gamma-ray logging data. Approximate locations of the studied structures (white) and boreholes (black points) are indicated on the map. Other onshore Latvian structures prospective for CGS (CO_2 storage potential exceeding 2 Mt) are shown in light grey.

CGS at depths of 800–2500 m, where CO_2 can be stored in a supercritical state (>31 °C and >73 atm). The geological conditions are most favourable in the uplifted structures in Latvia, where more than 30 anticlinal deep geological structures onshore and offshore Latvia, with different sizes and a storage capacity exceeding 2 Mt of CO_2, have been estimated as prospective for CGS (Sliaupa et al. 2008a; Shogenova et al. 2009a, 2009b, 2011a, 2011b; Shogenov et al. 2013a, 2013b; Šliaupa et al. 2013). Four geological structures, located onshore

(South Kandava and Dobele) and offshore Latvia (E6) and Lithuania (E7) and serving as prospective CGS sites in the Baltic Sea Region (Fig. 1), were previously described in detail by Shogenov et al. (2013a, 2013b).

The petrophysical properties and geochemical and mineralogical composition of 24 samples of the Deimena Formation reservoir and Zebre Formation cap rocks from four Baltic onshore and offshore structures were studied and analysed together with previously reported data. The properties of reservoir rocks, cross sections and 3D geological models, constructed using geophysical and geological data, were used for the estimation of the theoretical CO_2 storage capacity of these structures in our earlier studies. The selected structures have an average porosity of 12–21%, permeability of 40–360 mD and mean reservoir thickness of 42–58 m. The average CO_2 storage potentials ('conservative'–'optimistic') of the Dobele, South Kandava, E7 and E6 structures were, respectively, 20–106, 25–95, 7–34 and 152–377 Mt. We estimated the E6 offshore structure as the largest trapping structure prospective for CGS offshore Latvia with the highest CO_2 storage capacity (Shogenov et al. 2013a, 2013b). Based on exploration report data (Babuke et al. 1983), we have treated E7 as a Latvian offshore structure in our earlier publications (Shogenov et al. 2013a, 2013b). However, according to the new Latvian–Lithuanian territorial agreement in the Baltic Sea, signed by Prime Ministers of Latvia and Lithuania in 1999, the E7 structure belongs now to Lithuania (Šteinerts 2012).

DIAGENETIC MODIFICATION OF RESERVOIR PROPERTIES

The studied Cambrian rocks were subjected to different diagenetic conditions across the basin, with a wide spectrum of rock modification under shallow to deep burial conditions, reflected in growing clay mineral maturity with increasing depth, variations in the composition of sandstone cement, with authigenic quartz prevailing in the deep part of the basin and carbonate cements prevailing in the basin periphery, etc. The carbonate cement of sandstones is varying in mineralogy from common ferroan dolomite and ankerite to less common calcite and siderite (Sliaupa et al. 2008b). Quartz cementation that formed during the late diagenetic stage (Lashkova 1979; Sikorska & Paczesna 1997) and increases with depth is the main factor influencing the reservoir properties of rocks both in onshore and offshore structures.

Quartz is the main cement mineral, occurring in the form of authigenic overgrowths on detrital quartz grains (Lashkova 1979; Kilda & Friis 2002). According to Čyžienė et al. (2006), quartz cement is regionally widespread, but mainly confined to areas where present-day temperatures in the Cambrian are 50–90 °C. Sliaupa et al. (2008b) stated that quartz cementation started at 1 km depth. The amount of quartz cement increases towards the deeper buried parts of the basin in West Lithuania, but is highly variable on a local scale and even within individual structures. Quartz cement contents show a negative correlation with porosity (Čyžienė et al. 2006) and with carbonate cement (Sliaupa et al. 2008b).

Another diagenetic process negatively influencing the reservoir properties is compaction. Pore reduction by mechanical compaction is one of the main controls of the petrophysical properties of Cambrian sandstones. The importance of mechanical compaction in reducing porosity and causing lithification is stressed by Čyžienė et al. (2006). Compaction comprised the mechanical rearrangement of grains throughout the sandstones as well as the chemical compaction along shale–sandstone contacts and within shales. Grain breakage is rare and no intergranular pressure solution in clay-free clean sandstones has been observed. In sandstones detrital quartz grains mainly have point contacts. Differences in the degree of mechanical compaction are probably related to both maximum burial depth and variations in the depositional texture and susceptibility of sand to mechanical compaction.

REQUIREMENTS FOR RESERVOIR ROCKS

A typical reservoir for CGS is a geological formation consisting of sandstone or carbonate rock characterized by 'good' effective porosity and permeability. Effective (open) porosity is the porosity that is available for free fluids; it excludes all non-connected porosity, including the space occupied by clay-bound water (Schön 1996). The ranges of 'good' reservoir porosity and permeability for oil and gas reservoirs are 15–20% and 50–250 millidarcy (mD), respectively (Tiab & Donaldson 2012).

Until now there is no unified classification specifying requirements for 'high-', 'good-' or 'low-quality' reservoirs for CO_2 storage. As a general rule the formation permeability must exceed 200 mD for a specific reservoir to provide sufficient injectivity (Van der Meer 1993). However, the values greater than 300 mD are preferred and considered as positive indicators to start the screening process of the possible storage site (Chadwick et al. 2006; Vangkilde-Pedersen & Kirk 2009). The porosities should be larger than 20%, while those below 10% and permeability below 200 mD are considered 'cautionary' by these authors (Table 1). The cumulative thickness of reservoirs should be greater than 50 m. The reservoirs less than 20 m thick are

Table 1. Classification of the reservoir rocks according to permeability and porosity

Hydrocarbon reservoirs (Khanin 1965, 1969)					CO_2 storage standards*					Classification of the studied rocks for CO_2 storage**					
Group	Class	Reservoir quality	*K* (mD)	*Φ* (%)	Group	Class	Reservoir quality	*K* (mD)	*Φ* (%)	Group	Application for CGS	Class	Reservoir quality	*K* (mD)	*Φ* (%)
1	I	Very high	≥1000	≥20	1	I	High	>500	>25	1	Very appropriate	I	High-1	>300	≥20
							Preferred	>300	>20			II	High-2		9–20
	II	High	500–1000	18–20		II	Good	50–250	15–20	2	Appropriate	III	Good	100–300	>18
	III	Average	100–500	14–18		III	Moderate	50–250	10–15			IV	Moderate		9–18
2	IV	Reduced	10–100	8–14	2	IV	Cautionary	<200	<10	3	Cautionary	V	Cautionary-1	10–100	18–23
								<50				VI	Cautionary-2		7–18
	V	Low	1–10	2–8		V	Low	<10	<15	4	Not appropriate	VII	Low	1–10	7–18
	VI	Very low	<1	<2								VIII	Very low	<1	<18

* CO_2 storage standards modified after Van der Meer (1993), Chadwick et al. (2006), Vangkilde-Pedersen & Kirk (2009), Tiab & Donaldson (2012), Halland et al. (2013): group 1, acceptable for CGS; group 2, cautionary.
** New classification based on the studied data (reported and measured in laboratory before the alteration experiment), proposed by the authors for the studied region and geological structures. *K*, gas permeability; *Φ*, porosity.

considered unsuitable for the storage of large amounts of CO_2. According to Halland et al. (2013), a homogeneous 50 m thick reservoir with a permeability >500 mD and porosity >25% is estimated as a 'high-quality' reservoir, while heterogeneous 15 m thick reservoir with a permeability <10 mD and porosity <15% is considered as a 'low-quality' reservoir for CGS.

The classification of hydrocarbon reservoirs proposed by Khanin (1965, 1969) was used during exploration for hydrocarbon deposits on the territory of the Baltic States and later for the characterization of petroleum geology in the region (Zdanavičiute & Sakalauskas 2001). Based on porosity and permeability, Khanin divided hydrocarbon reservoirs into six classes without any overlapping of these parameters in reservoir quality classes (Table 1). In his classification the hydrocarbon reservoirs of 'high' and 'very high' quality have a permeability more than 500 and 1000 mD, respectively, while requirements for porosity (18–20 and >20%) are close to the positive indicators for CO_2 storage reservoirs (>20%) given by Chadwick et al. (2006) and Vangkilde-Pedersen & Kirk (2009).

CO_2–RESERVOIR ROCK INTERACTION

When injected into the aquifer or water-flooded oil reservoir, CO_2 has an impact on the pH level of in situ brine, modifying it into a more acidic state. Isotope studies of natural analogues of CO_2 reservoirs suggest that the dissolution of CO_2 in formation brine is the main phenomenon in the long term, causing the acidification of native brine to a pH of approximately 3–5 (Gilfillan et al. 2009; Liu et al. 2011, 2012). Chemically, this simple acid reaction is illustrated by equation (1), showing the formation and dissociation of carbonic acid ($H_2CO_3^0$) from dissolved CO_2 in formation brine:

$$CO_2 + H_2O \leftrightarrow H_2CO_3^0 \text{ (carbonic acid)} \leftrightarrow H^+ + HCO_3^-. \quad (1)$$

Acidic brine then reacts with the solid matrix of reservoir sediments (i.e. calcite, dolomite and anhydrite):

$$H^+ + HCO_3^- + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \text{ Calcite dissolution/ precipitation.} \quad (2)$$

This exact phenomenon, induced by CO_2 injection into the aquifer, was applied as the main factor of the experiment and is a basis for further research.

A number of recent papers have been dedicated to CO_2–brine–host reservoir rock interactions, both for sandstones and carbonate rocks (Ross et al. 1982; Svec & Grigg 2001; Grigg & Svec 2003; Rochelle et al. 2004; Bertier et al. 2006; Czernichowski-Lauriol et al. 2006;

Egermann et al. 2006; Pawar et al. 2006; Izgec et al. 2008; Bemer & Lombard 2010; Carroll et al. 2011, 2013; Nguyen et al. 2013).

The CGS-related laboratory experiments, numerical modelling and field monitoring of CO_2 storage sites have shown both partial dissolution and precipitation of various minerals. A simplified equation for minor mineral dissolution/precipitation of host rock was given by Hitchon (1996):

Ca/Mg/Fe silicate + clays + CO_2 + H_2O → kaolinite + Ca/Mg/Fe carbonate + quartz. (3)

The reaction of carbonic acid with aluminosilicate or carbonate minerals produces significant alkalinity (Kaszuba & Janecky 2009):

$2KAlSi_3O_8$ (K-feldspar) + $2H_2CO_3$ (carbonic acid) + $9H_2O$ → $Al_2Si_2O_5(OH)_4$ (kaolinite) + $4H_4SiO_4$ (silicic acid) + $2K^+$ + $2HCO_3^-$(bicarbonate), (4)

$CaMg(CO_3)_2$ (dolomite) + $2H_2CO_3$ (carbonic acid) → Ca^{2+} + Mg^{2+} + $4HCO_3^-$(bicarbonate). (5)

The alkalinity of in situ brine cannot overcome the acidity within the repository that was produced by the dissolution of supercritical CO_2 fluid. However, due to the separation of brine from supercritical CO_2 and the prevailing chemical potential of carbonic acid, alkalinity in brine can neutralize the acidity, yielding near-neutral pH (Kaszuba & Janecky 2009).

Gilfillan et al. (2008, 2009) studied stable carbon $\delta^{13}C$ (CO_2) isotope tracers from natural CO_2-bearing siliciclastic and carbonate gas reservoirs around the world. They explored CO_2 dissolution into formation brine at various pH values as the primary sink for CO_2 and precipitation of CO_2 as carbonate minerals. Nevertheless, this process is very site- and condition-dependent and, in several cases, no important rock–fluid interaction impact on the petrophysical properties of the reservoir host rocks has been reported (Prieditis et al. 1991; Kamath et al. 1998).

MATERIAL AND METHODS

The porosity (Φ) and gas permeability (K) data of 115 samples, including those from six drill cores (E6-1/84, E7-1/82, South Kandava 24 and 27, Dobele 91 and 92) described in old exploration reports (Silant′ev et al. 1970; Dmitriev et al. 1973; Babuke et al. 1983; Andrushenko et al. 1985), from the Liepaja-San borehole (GEOBALTICA project, Shogenova et al. 2009a) and the ones recently measured in IFP Energies nouvelles (IFPEN, French Petroleum Institute, Paris) (Shogenov et al. 2013a, 2013b), were used for the classification of the reservoir quality of sandstones. Gas permeability was calculated as an average value of reported permeability measured in horizontal and vertical directions. A more detailed description of permeability measurements from the Liepaja structure (Liepaja-San borehole) is given in Shogenova et al. (2009a). The physical properties of 139 samples from seven boreholes (offshore E6-1/84 and E7-1/82, onshore South Kandava 24 and 27, Dobele 91 and 92, Liepaja-San), measured recently or reported earlier, were used in this study. The K values of 127 samples and Φ values of 128 samples, grain density of 102 samples, bulk density of 129 dry samples, P-wave velocity (V_P) in 60 dry samples and S-wave velocity (V_S) in 10 dry samples comprised the recent and earlier data (Shogenova et al. 2001b; Shogenov et al. 2013a, 2013b).

Twelve rock samples of the reservoir sandstones of the Deimena Formation from four boreholes drilled onshore in the South Kandava structure and offshore in the E6 and E7 structures (Fig. 1, Table 1) and stored in the Latvian Environmental, Geological and Meteorological Centre were used for the CO_2 injection-like alteration experiment conducted at the IFPEN. Detailed descriptions of the methods applied are available in Shogenov et al. (2013a, 2013b). Bulk and grain helium density, helium porosity, gas permeability and acoustic wave velocities in dry samples, the chemical and mineralogical composition and surface morphology were studied in the 12 selected rocks both before and after the experiment. Due to partial destruction of several samples during the experiment, it was possible to measure K values in 11, V_P in nine and V_S in three samples. The total chemical composition of the samples was measured by X-ray fluorescence (XRF) analysis by Acme Analytical Laboratories Ltd. before and after the alteration experiment. CaO, MgO and insoluble residue (IR) were measured by the titration geochemical method only before the experiment. Thin sections of the samples were studied in the Institute of Geology at Tallinn University of Technology (IG TUT) using a Scanning Electron Microscope (SEM) equipped with an energy dispersive spectrometer (EDS). The thin sections were made after the experiment from the rock–fluid contact zone where alteration was confirmed by the high solubility of the samples. Due to partial destruction of some rocks, the weight of the samples was measured both before and after the experiment.

The CO_2 injection part in our experiment was simplified to consider only the impact on the contact area between acidified fluid and the studied rocks. This simplification ensures a homogeneous distribution of brine on the core scale and allows us to avoid very local ‘worm-holing’ effects on samples and erroneous physical measurements (Egermann et al. 2006; Bemer & Lombard 2010). The homogeneous alteration method, or retarded acid approach, was conducted at IFPEN. It constitutes in the placement of samples into the Hastelloy cell maintained under vacuum conditions and injection of an acid solution. Acid treatment was performed at 10 bar pressure and temperature of 60 °C (for at least one day), simulating CO_2-rich brine in an aquifer characterized by lowered pH (approximately three units). This method has been developed and described in detail in Egermann et al. (2006) and Bemer & Lombard (2010). The day after, each sample was placed in a 25-mm-diameter cell and flooded by three pore volumes of 20 g L^{-1} NaCl brine at 20 °C to stop the weathering. After this flooding the samples were dried in an oven for three days. The procedure was repeated three times.

Siliciclastic rock samples with good reservoir properties are often weakly cemented. In order to keep their regular shape in the experiments involving the flushing of samples with supercritical CO_2 and brine, the use of samples of various sizes and shapes was allowed by the implemented alteration method.

EXPERIMENTAL AND INTERPRETATION UNCERTAINTIES

Experimental uncertainties include the quality control of petrophysical measurements. To distinguish between a real trend in a data set and variation due to the experimental uncertainty, the American Petroleum Institute (API 1998) has recommended reporting core analyses data together with a statement of the uncertainty with which these data were recorded.

Variations in the permeability and acoustic velocity measurements were quite high in the presented study due to the sample sizes that differed from the standard ones at the IFPEN petrophysical and petroacoustic laboratories. The standard samples were 40 mm in diameter and 80 mm in length, thus the length/diameter ratio should be higher or equal to two (Egermann et al. 2006). The studied samples were 25 mm in diameter and 11–27 mm long. Therefore, the experimentally established accuracy (using replicate measurements of each sample) was 20% for the *K* values, and 10% for P- and S-wave velocity measurements for the used petroacoustic installations.

The accuracy of grain density measurements was <0.7%. It consisted of an analytical balances (from Mettler Toledo) accuracy of 0.2% (estimated experimentally) and less than 0.5% pycnometer accuracy for sample solid volume measurements (AccuPyc from Micromeritics), given as the default error. The accuracy of bulk density measurements due to the balances accuracy (0.2%) and GeoPyc pycnometer (from Micromeritics) for the estimation of the total sample volume with reported default accuracy of 1.5% was 1.7%. The porosity measurements, supported by the high accuracy pycnometers from Micromeritics (GeoPyc and AccuPyc with 1.5% and 0.5% accuracy, respectively), provided a total of 2% accuracy.

The uncertainties and variations due to the accuracy of the measurements of altered petrophysical parameters and possible mistakes caused by changes in the sizes and shapes of rock samples were checked using well-known relationships: bulk density–porosity and acoustic velocity–porosity negative correlations; permeability–porosity positive correlation in general and available scatter from this relationship for the sandstones of the Deimena Formation in the studied region; and acoustic velocity–matrix and bulk density positive correlations (Schön 1996; Sliaupa et al. 2001; Mavko et al. 2003; Shogenova et al. 2009a).

RESULTS

Assessment of the quality of the reservoir rocks

Considering the permeability and porosity requirements for CO_2 geological storage (Van der Meer 1993; Chadwick et al. 2006; Vangkilde-Pedersen & Kirk 2009; Tiab & Donaldson 2012; Halland et al. 2013), hydrocarbon reservoir classification by these parameters proposed by Khanin (1965, 1969) and earlier and recent data of 115 sandstone samples (Shogenova et al. 2009a; Shogenov et al. 2013a, 2013b), we subdivided the reservoir sandstones of the Deimena Formation into four groups and eight classes based on reservoir quality (Tables 1, 2, Fig. 2). The groups were distinguished using the permeability limits of 300, 100, 10 and 1 mD. Each group was subdivided into two classes of various porosity. The reservoir rocks of the first group that are 'very appropriate' for CGS, having the highest permeability and high porosity, were subdivided into 'high-1' (porosity ≥20%) and 'high-2' (porosity 9–20%) quality classes I and II, respectively. The second group, 'appropriate' for CGS, composed of rocks with a permeability of 100–300 mD, was subdivided into 'good' and 'moderate' quality classes III and IV (porosity >18% and 9–18%, respectively). The third group, 'cautionary' for CGS, contains rocks with a permeability of 10–100 mD and was subdivided into 'cautionary-1' and 'cautionary-2' classes V and VI (porosity 18–23% and 7–18%, respectively). The last group, 'not appropriate' for CGS, comprises rocks with a permeability <10 mD. It was subdivided into 'low' and 'very low' quality classes VII and VIII. Class VII comprises rocks with a permeability of 1–10 mD and porosity 7–18%, and class VIII contains rocks with a permeability <1 mD and porosity <18%.

Table 2. Average properties of the sandstones of the Deimena Formation before the alteration experiment

Group	Class	Reservoir quality	*K* (mD) min–max/mean(*N*)	*Φ* (%) min–max/mean(*N*)	Grain density (kg m^{-3}) min–max/mean(*N*)	Bulk density dry (kg m^{-3}) min–max/mean(*N*)
1	I	High-1	334–763/525(11)	20.1–25.8/22.3(10)	2670–2718/2694(10)	1807–2150/2034(11)
	II	High-2	347–600/440(9)	12.5–19.2/17.2(10)	2680–2730/2707(10)	2110–2260/2167(10)
2	III	Good	113–295.5/183(17)	19–25.5/22.5(17)	2680–2725/2700(2)	1980–2130/2050(17)
	IV	Moderate	102–261/186(8)	12–17.8/14.8(8)	2640–2750/2693(6)	2200–2330/2274(8)
3	V	Cautionary-1	33–84/62(12)	18.5–22.9/20.8(12)	2630–2720/2677(6)	2020–2310/2133(12)
	VI	Cautionary-2	16–94/45(41)	8.5–16.2/12.1(41)	2600–2820/2661(39)	2250–2430/2334(41)
4	VII	Low	1.5–10/6.2(8)	7.95–17.5/13.1(8)	2660–2730/2683(7)	2210–2450/2315(8)
	VIII	Very low	0.001–0.7/0.2(10)	0.8–16.3/8.9(10)	2664–2840/2712(10)	2200–2780/2452(10)

K, gas permeability; *Φ*, porosity; min, minimum; max, maximum; mean, average; *N*, number of studied samples (measured and reported).

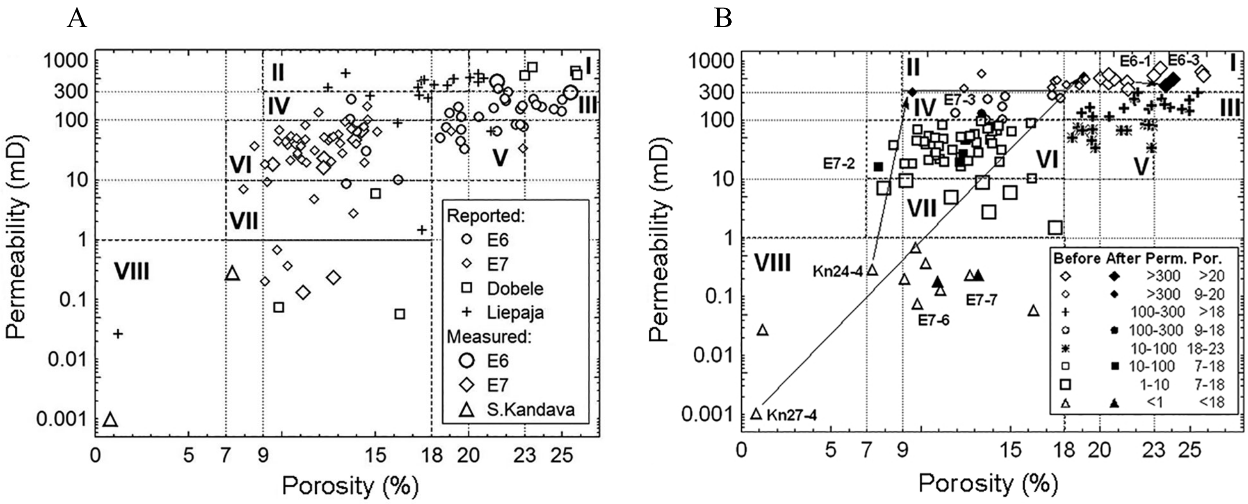

Fig. 2. Gas permeability versus porosity of the reported and measured sandstones of the Deimena Formation from two offshore and three onshore structures in eight reservoir quality classes I–VIII (Tables 1, 2) based on: (**A**) 115 samples reported and measured before the alteration experiment in terms of five structures; (**B**) 115 samples reported and measured before the alteration experiment (empty symbols) and 12 samples measured after alteration (black symbols) in terms of eight reservoir quality classes. Perm., gas permeability; Por., porosity.

Every reservoir quality class is characterized by a unique set of petrophysical parameters. However, rocks in groups one and two, 'very appropriate' and 'appropriate' for CGS, respectively, differ mainly in permeability, but have a common range of porosities, determining their similarities in other physical properties (Tables 1, 2).

The first group, 'very appropriate' for CGS (classes I and II), includes samples from the offshore E6, onshore Dobele-92 and Liepaja-San boreholes.

The second group, 'appropriate' for CGS, class III, is composed of rocks from the E6-1/84 borehole, while class IV also includes rocks from the E7-1/82 and Liepaja-San boreholes.

The third group, 'cautionary' for CGS, 'cautionary-1' class V, includes samples mainly from the E6-1/84 borehole, while 'cautionary-2' class VI contains mostly rocks from the E7-1/82 borehole.

The last, 'very low' reservoir quality class VIII from the fourth group, 'not appropriate' for CGS, includes clay-cemented samples from the E7 structure and carbonate-cemented samples from the South Kandava structure, supplemented by three samples from the Dobele and Liepaja structures (Fig. 2A). Class VII includes the samples (E6, E7, Liepaja and Dobele structures) which had higher permeability and porosity, lower grain and bulk density and P-wave velocity than the rocks of class VIII.

Assessment of the reservoir quality of sandstones before and after alteration

According to the chemical and lithological classification proposed by Shogenova et al. (2005, 2006), sample Kn27-4 is a mixed carbonate-siliciclastic sandstone (50 < IR < 70%), while the other studied samples (E6-1–E6-3, E7-1–E7-7 and Kn24-4) are siliciclastic sandstones (IR > 70%) of different quality, clay and carbonate cement content (Table 3).

According to our classification based on permeability and porosity (Table 1), offshore sandstones from the E6 structure are mainly of ‘good’ and ‘high-1’ reservoir quality (classes III and I, respectively), with a small number of samples of ‘cautionary-1’ class V and rare samples of classes IV, VI and VII. Offshore sandstones from the E7 structure are mainly of ‘cautionary-2’ reservoir quality class VI, while rest of the samples belong to classes IV–VII. Clay-cemented samples from the downward part of the E7 reservoir (70 < SiO_2 < 90% and Al_2O_3 > 5%, Table 3) and carbonate-cemented samples (65 < SiO_2 < 85% and CaO > 5%, Table 3) from the upward part of the onshore South Kandava structure are in ‘very low’ quality class VIII.

The ‘high-1’ and ‘good’ reservoir quality (classes I and III, respectively) quartz sandstones from the E6 structure are mainly composed of quartz, with minor amounts of clay (illite and/or kaolinite) and carbonate cement forming minerals, admixture of feldspar and accessory minerals represented by pyrite, barite, anatase and/or brookite and zircon (Shogenov et al. 2013a, 2013b). Increase in effective porosity, supported by decrease in bulk and grain density, and slight decrease in sample weight, due to the dissolution of minor carbonate cement, displacement of clay cement after the experiment and minor increase in microfractures in grains, were determined after the alteration experiment in the samples from this structure (Tables 3, 4, Figs 3, 4). However, the changes in permeability and porosity did not cause a significant change in their reservoir quality and samples from the E6 structure remained in the same ‘high-1’ and ‘good’ reservoir quality classes after the experiment (Table 4, Fig. 2).

The sandstones from the E7 offshore structure are also mainly composed of quartz. Compared to sandstones present in the E6 structure, sandstones in the E7 structure in some parts of the Deimena Formation contain more clay and carbonate minerals, including ankerite, dolomite, admixture of feldspar and clay fraction represented by kaolinite and illite. Sandstones in the upper part of the Deimena Formation are mostly cemented by quartz-generated cement. Rocks in the lower part of the formation are characterized by conformation of quartz grains due to dissolution under pressure (Shogenov

Table 3. Chemical composition of the sandstones of the Deimena Formation before and after the alteration experiment (major oxides and insoluble residue)

Sample	Depth (m)	Wet chemical analysis (%)			XRF analysis (%)									
		IR	CaO	MgO	SiO_2		CaO		MgO		Al_2O_3		Fe_2O_3	
		Before alteration			Before	After	Before	After	Before	After	Before	After	Before	After
E6-1	860.4	97.14	0.88	0.24	97.8	97.0	0.07	0.03	0.03	0.02	0.24	0.70	0.06	0.06
E6-2	886.7	97.44	1.10	0.24	97.4	94.8	0.10	0.03	0.04	0.04	0.34	1.30	0.16	0.09
E6-3	886.7	97.44	1.10	0.24	97.4	95.7	0.10	0.03	0.04	0.03	0.34	1.10	0.16	0.07
E7-1	1387.6	97.12	1.10	0.24	98.7	98.6	0.05	0.02	0.02	<0.01	0.27	0.72	0.08	0.02
E7-2	1389.5	98.64	0.88	0.33	98.3	98.7	0.04	0.02	0.01	<0.01	0.38	0.70	0.06	0.03
E7-3	1390.5	97.16	1.10	0.49	97.6	98.3	0.30	0.13	0.11	0.07	0.27	0.61	0.19	0.09
E7-4	1390.5	97.16	1.10	0.49	97.6	98.7	0.30	0.11	0.11	0.06	0.27	0.84	0.19	0.14
E7-5	1393.2	97.86	1.10	0.41	97.8	98.4	0.04	0.02	0.03	<0.01	0.59	0.72	0.31	0.06
E7-6*	1394.2	93.60	1.54	0.49	87.2	90.2	0.16	0.05	0.34	0.20	5.26	4.96	1.85	1.10
E7-7*	1394.2	93.60	1.54	0.49	87.2	86.4	0.16	0.07	0.34	0.33	5.26	6.63	1.85	1.54
Kn24-4**	1157.3	80.64	6.38	2.12	81.1	85.4	5.61	3.95	1.98	1.40	0.26	0.43	2.32	1.74
Kn27-4**	998.8	68.04	16.5	0.57	70.0	75.0	15.69	12.23	0.12	0.23	0.18	0.34	0.13	0.09

Before, samples measured before the alteration experiment; after, samples measured after the alteration experiment; * clay-cemented; ** carbonate-cemented sandstones from the South Kandava structure; IR, insoluble residue.

Table 4. Reservoir quality classes and petrophysical properties of sandstones of the Deimena Formation studied in the alteration experiment

Sample	Depth (m)	Reservoir quality class		Weight (kg 10^{-3})		Bulk density (kg m^{-3})		Grain density (kg m^{-3})		Porosity (%)		Permeability (mD)		V_P ($m\ s^{-1}$)		V_S ($m\ s^{-1}$)	
		Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
E6-1	860.4	I	I	17.6	**17.5**	2123	**2011**	2705	**2635**	21.5	**23.7**	440.0	*380.0*	–	2310	–	–
E6-2	886.7	III	III	12.0	*6.4**	2031	**1863**	2725	**2661**	25.5	**30.0**	290.0	**–**	–	–	–	–
E6-3	886.7	I	I	10.2	**10.0**	–	**1999**	2718	**2633**	–	24.1	400.0	**490.0**	–	–	–	–
E7-1	1387.6	VI	VI	16.8	**16.7**	2354	**2310**	2683	**2636**	12.3	*12.4*	23.0	*26.0*	3583	*3300*	–	–
E7-2	1389.5	VI	VI	26.5	*26.5*	2412	*2439*	2666	**2641**	9.5	**7.7**	18.0	*16.0*	2457	*2280*	1725	–
E7-3	1390.5	VI	IV	24.8	**24.6**	2309	*2295*	2693	**2650**	14.3	**13.4**	66.0	**130.0**	3096	**2750**	2194	**1850**
E7-4	1390.5	VI	VI	15.6	**15.5**	2339	**2284**	2716	**2653**	13.9	*13.9*	46.0	**78.0**	–	–	–	–
E7-5	1393.2	VI	VI	24.9	*24.8*	2349	*2323*	2676	**2646**	12.2	*12.2*	16.0	*19.0*	3097	*3100*	2230	*2020*
E7-6*	1394.2	VIII	VIII	24.7	**24.3**	2403	*2367*	2704	**2659**	11.1	*11.0*	0.13	**0.18**	2524	**1230**	–	–
E7-7*	1394.2	VIII	VIII	24.8	*16.1**	2395	**2322**	2746	**2676**	12.8	**13.3**	0.23	*0.23*	2130	*2130*	–	–
Kn24-4**	1157.3	VIII	IV	35.3	**31.6**	2642	**2148**	2741	**2675**	7.3	**9.6**	0.28	**300.0**	4556	**4030**	3225	–
Kn27-4**	998.8	VIII	II	35.0	**27.1**	2539	**2419**	2664	*2658*	0.8	**19.1**	0.001	**550.0**	5400	**4380**	3600	**2540**

Before, samples measured before the alteration experiment; after, samples measured after the alteration experiment; V_P, P-wave velocity; V_S, S-wave velocity; * clay-cemented; ** carbonate-cemented sandstones from the South Kandava structure.
Bold and *italic* numbers in the table correspond, respectively, to 'reliable' and 'not reliable' changes in petrophysical parameters after the alteration experiment according to measurement errors. 'Not reliable' values also correspond to the parameters not subjected to alteration.

et al. 2013a, 2013b). Reliable changes in the physical properties of rock were detected in the nearly pure (estimated by XRD) quartz sandstones E7-2–E7-5, sampled from the depth interval 1389.5–1393.2 m (Table 4; Figs 2, 5). The grain density in these samples and the effective porosity in samples E7-2 and E7-3 were found to decrease. A reliable decrease in weight and a significant increase in permeability were detected in sample E7-3 (Fig. 6). Additionally, a reliable decrease in P- and S-wave velocity was determined in sample E7-3. A reliable decrease in bulk density was recorded only in sample E7-4 (Table 4). However, the only sample E7-3 from class VI ('cautionary-2') improved its reservoir quality up to class IV ('moderate') owing to its permeability increase, while the quality of the other samples was not improved after the experiment.

Only slight decrease in sample weight and grain density, and a significant reduction in P-wave velocity, supported by some insignificant variations in permeability and porosity, were determined in clay-cemented sandstones E7-6 and E7-7 of initially 'very low' quality class VIII. After the alteration both samples remained in the same reservoir quality class (Table 4, Fig. 2).

The transitional reservoir (trans-res) sandstones from the South Kandava onshore structure (located 0.2–0.3 m below the Lower Ordovician cap rock formation) are characterized by a higher carbonate cement content than the other studied pure reservoir sandstones. Trans-res sandstone Kn24-4 (0.3 m below the cap rock formation, Figs 1, 7) was estimated by XRD and XRF analyses as ankerite-cemented almost pure quartz sandstone of 'very low' reservoir quality (class VIII). Sample weight decreased after the alteration experiment due to the dissolution of cement (expressed by a decrease in CaO content from 5.61% before to 3.95% after alteration, Table 3). Also bulk and grain density and P-wave velocity decreased, associated with a significant rise in effective porosity and drastically increased permeability (Table 4, Figs 2B, 3B, 5). Thin section study confirmed the results of the physical measurements of rock, showing the dissolution and microfracturing of carbonate cement and the displacement of clay cement, which previously blocked pores, after alteration (Fig. 7). Owing to drastic changes in porosity and permeability, the reservoir quality of this rock sample was improved up to 'moderate' reservoir quality class IV 'appropriate' for CGS (group 2, Table 4).

Trans-res rock sample Kn27-4 (0.2 m below the cap rock formation, Figs 1, 8) was estimated by XRD analysis as sandstone with abundant quartz and minor calcite (mixed carbonate-siliciclastic rock by geochemical interpretation) and was assigned to 'low' reservoir quality (class VII). Sample weight decreased after the experiment

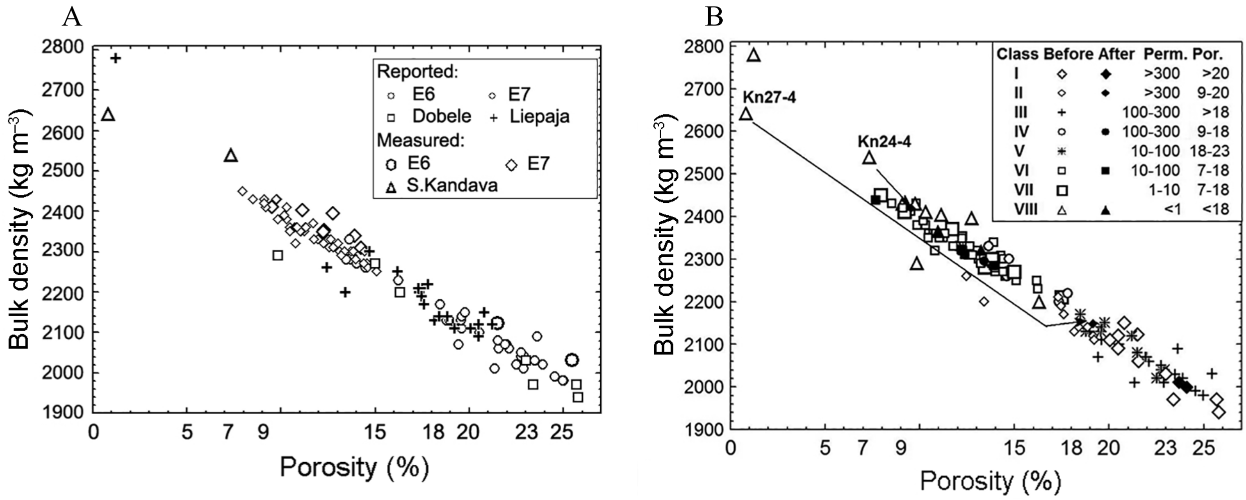

Fig. 3. Bulk density measured on dry samples versus porosity of the sandstones of the Deimena Formation from two offshore and three onshore structures: (**A**) for 115 samples reported and measured from seven boreholes before alteration; (**B**) for 115 samples reported and measured before alteration (empty symbols) and 12 samples measured after alteration (black symbols) in terms of reservoir quality classes I–VIII (Tables 1, 2). Perm., gas permeability; Por., porosity.

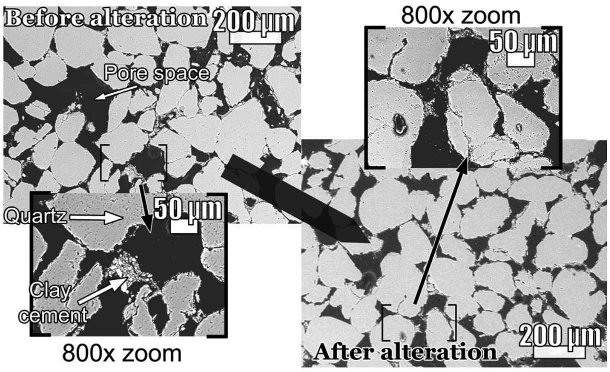

Fig. 4. SEM microphotographs of thin sections of reservoir fine-grained poorly sorted Deimena Formation sandstone sample E6-3 (Table 3) before (left) and after (right) the alteration experiment. The composition is oligomictic, characterized by predominantly subrounded to subangular quartz grains. Clay cement indicated on zoomed photos locally blocks porous media and accounts for about 5%. Open porosity is mostly interparticle, locally also intraparticle. The measured porosity of E6-3 after the alteration experiment (24.1%) was confirmed by visual analysis of thin sections (20–30% by Shvetsov 1948, Table 4). Slightly increased permeability (Table 4) could be explained by the dissolution of minor carbonate cement (Table 3), displacement of clay cement after the experiment and minor increase in microfractures in grains (right part). Sample E6-3 is of 'high-1' (class I) reservoir quality sandstone, very appropriate for CGS with no changes in the reservoir quality after the experiment.

due to partial dissolution of carbonate cement (expressed by a decrease in CaO content from 15.69% before to 12.23% after alteration, Table 3). It was accompanied by reduction in P- and S-wave velocity and bulk density, associated with dramatically increased effective porosity and permeability induced by chemical alteration (Table 4, Figs 2B, 3B, 5, 8). This caused an improvement of the reservoir quality of this sample up to 'high-2' reservoir quality class II, 'very appropriate' for CGS (group 1).

DISCUSSION

This study provides a set of experimental data concerning the change in the petrophysical properties of rocks under chemical alteration. The presented results do not allow yet the definition of constitutive laws taking the chemomechanical coupling into account.

The permeability of the studied sandstones varies by six orders of magnitude and by four orders of magnitude at a single porosity. At the same time the porosity of these sandstones varies in the range of 0.8–25.8% and can vary 2–2.5 times for a single permeability. Porosity and permeability are related to different properties of pore space geometry. This explains the correlation between porosity and permeability, but also the scattering of such correlations indicating strong additional influences (Schön 1996).

Great variability of the porosity of Cambrian sandstones in the Baltic Basin is explained by variation in their composition, grain size and sorting, pore structure, cementation, diagenetic alteration, burial depth and compaction, tectonic and geothermal conditions, and variation in onshore and offshore facies, especially in the northern and southern parts of the basin. As the

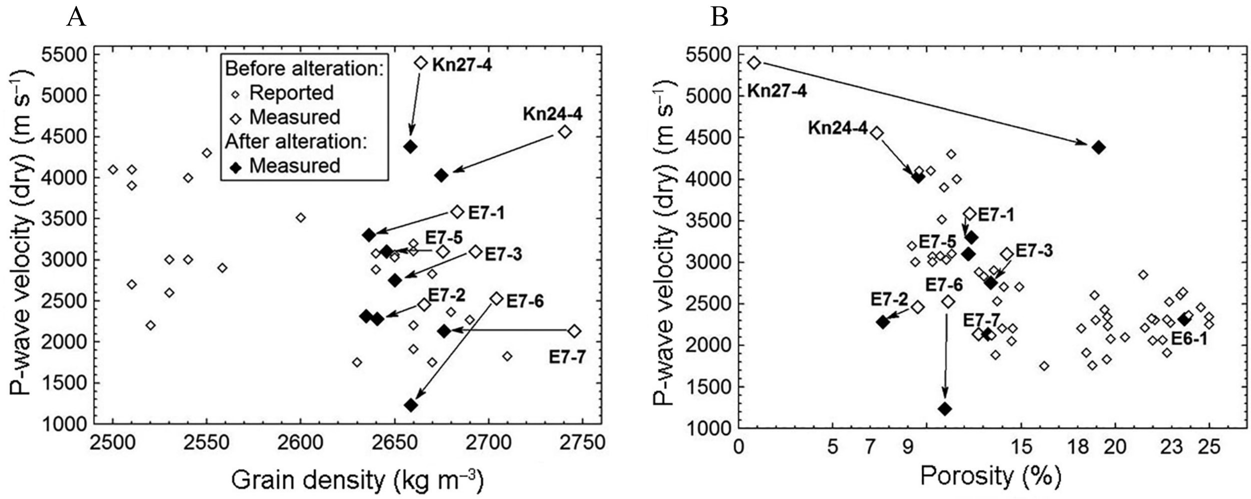

Fig. 5. (**A**) P-wave velocity versus grain density in dry sandstones of the Deimena Formation, reported (27 samples), and measured before (8 samples) and after (9 samples) the alteration experiment; (**B**) P-wave velocity versus porosity in dry sandstones, reported (52 samples), and measured before (8 samples) and after (9 samples) the alteration experiment (for legend see Fig. 5A). A decrease in the grain density in all samples and a decrease in the velocity in most of the samples were determined after the experiment.

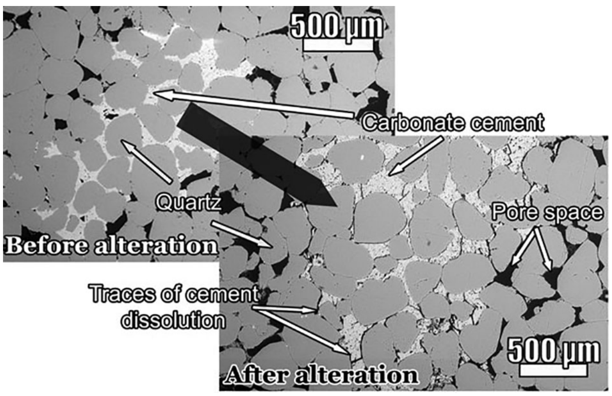

Fig. 6. SEM microphotographs of thin sections of reservoir carbonate-cemented medium- to fine-grained well-sorted Deimena Formation sandstone sample E7-3 (Table 3) before (left) and after (right) the alteration experiment. The sandstone composition is oligomictic, characterized by predominantly subrounded quartz grains. The sample is characterized by tight compaction of grains. Interparticle porosity is connected by very thin intermediate channels responsible for low permeability before alteration (Table 5). Visual analysis of thin sections (left and right) confirmed the measured results (10–15% by Shvetsov 1948, Table 5). The light-coloured area is carbonate cement (calcite, ankerite and dolomite), locally making more than 50% of the rock pore volume. Traces of the dissolution and microfracturing of carbonate cement on the edges of grains and inside the pore filling and the displacement of clay cement blocking pores were determined after the experiment (right). Increase in microporosity is responsible for increase in permeability measured after alteration (Table 5). Sample E7-3 is of ‘cautionary-2’ reservoir quality (class VI) with improved quality up to ‘moderate’ (class IV) after alteration.

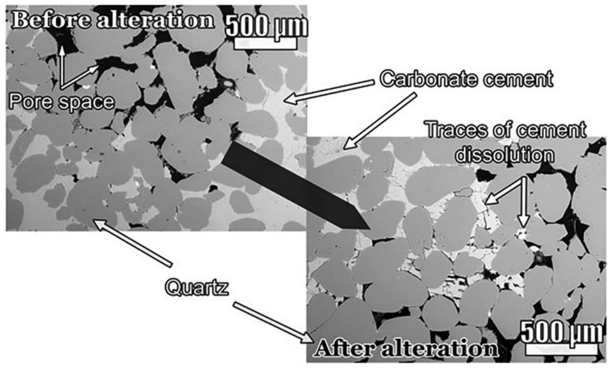

Fig. 7. SEM microphotographs of thin sections of trans-reservoir carbonate-cemented medium-grained poorly sorted Deimena sandstone sample Kn24-4 (Table 4) before (left) and after (right) the alteration experiment. The composition is oligomictic, predominantly characterized by subrounded quartz grains. XRD analyses revealed very minor presence of ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$) minerals. The light-coloured area is pore filling ankerite cement, occupying more than 50% of pores in the thin section. The presence of about 5% clay-supported matrix was determined before the alteration experiment. Clay-supported matrix is locally blocking interparticle porous media (left). The porosity has very thin intermediate channels responsible for very low permeability before alteration. Visual analysis of thin sections confirmed the measured porosity (5–10% by Shvetsov 1948, Table 4). Traces of the dissolution and microfracturing of carbonate cement on the edges of grains and inside the pore filling and displacement of the clay-supported matrix blocking pores after the experiment were determined (right). This phenomenon explains drastically increased permeability measured after alteration (Table 4). Sample Kn24-4 was of ‘very low’ reservoir quality before the alteration experiment and became of ‘moderate’ reservoir quality (class IV) after the experiment.

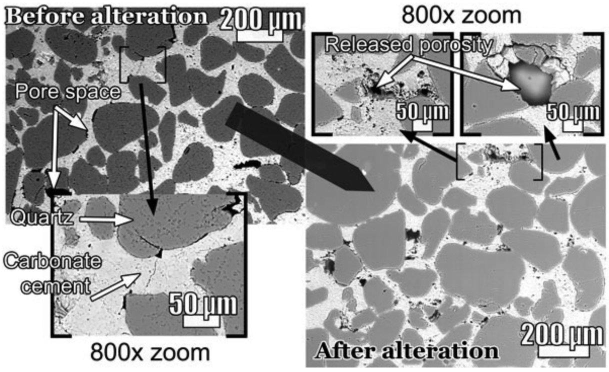

Fig. 8. SEM microphotographs of thin sections of trans-reservoir carbonate-cemented sample Kn27-4 from medium- to very fine-grained (fine-grained in general) unsorted Deimena sandstone (Table 3) before (left) and after (right) the alteration experiment. The composition is oligomictic, characterized by predominantly subrounded–subangular quartz grains. XRD analyses revealed minor calcite. The white-coloured area is pore filling calcite cement (carbonate), occupying almost 100% of pore space in the thin section. The appearance of new pores, which take up 1–5% of intragrain volume, was determined before the alteration experiment (left). Visual analysis confirms laboratory measurement data (Table 5). The zoomed image (lower left) of the thin section before alteration shows very thin interconnections between pores within carbonate cement, which makes the propagation of gases and liquids almost impossible (permeability = 0.001, Table 5). Spotted dissolution of cement with the destruction of cement matrix and locally quartz grains was observed after alteration (right). This phenomenon is responsible for drastically increased porosity and permeability after alteration (Table 5). Sample Kn27-4 was of 'very low' reservoir quality sandstone. During the alteration experiment its reservoir quality improved up to 'high-2' (class II), 'very appropriate' for CGS (Table 1).

studied sandstones of the Deimena Formation are located in the central middle part of the Baltic Cambrian Basin (700–1700 m depth), transitional from its northern shallow to southern deep part, they could have properties of both parts of the basin. However, even the porosity and permeability of uncompacted Cambrian sandstones from the shallow part of the basin range from very low values (1.5% and 0.001 mD, respectively), due to a high share of carbonate cement, to some 40% and 1300 mD in weakly cemented rocks (Shogenova et al. 2009a). The porosity of sandstones in the southwestern deep Lithuanian part of the basin (>1700 m) is mostly lower than that in carbonate- and clay-cemented sandstones in the shallow and middle parts of the basin, ranging within 0.4–12.4%. This is explained by compaction and secondary quartz cementation. However, the permeability of rocks in the southern part is varying in a rather wide range (0.003–960 mD) (Sliaupa et al. 2001, 2008b; Čyžienė et al. 2006; Shogenova et al. 2009a). Considering these porosity and permeability ranges, the classification of the reservoir rocks for CO_2 storage (Table 1), proposed in this research for the middle Latvian–Lithuanian parts of the basin (700–1700 m depth), could be adopted to shallow and deep parts of the basin with some possible corrections of porosity ranges for the reservoir quality classes in the deep part.

The initial permeability and porosity of the sandstones studied in the experiment were mainly controlled by the amount and type of diagenetic cement. Sandstones of 'very low' reservoir quality class VIII with the highest content of carbonate and clay cement had the lowest permeability (0.001–0.7 mD). The porosity of carbonate-cemented sandstones with the given permeability was lower than in clay-cemented samples (Tables 1, 3, Fig. 2). This corresponds to the results reported for the northern shallow part of the basin, where carbonate cementation has higher influence on the reduction of the porosity of Cambrian sandstones than clay cement, and grain-size influences the porosity of these rocks to a lesser degree than cementation (Shogenova et al. 2001a).

In sandstones from the offshore Lithuanian E7-1/82 and Latvian E6-1/84 boreholes, characterized by the same amount of clay and carbonate cement, lower permeability and porosity values were detected in the more compacted sandstones from the deeper E7 structure (class VI). Our study revealed different rock microstructure of sandstones of the Deimena Formation. For example, sandstone from the E6 structure (E6-3, Fig. 4) was characterized in general by fine grain size (0.25–0.125 mm, Krumbein phi scale, Krumbein 1934), poor sorting of the material and clay cement content of 5%. Sandstone from the E7 structure (E7-3, Fig. 6) is medium- (0.5–0.25 mm) to fine-grained, well-sorted with a high content of carbonate cement (about 50%). Sandstones from the South Kandava structure are medium- to very fine-grained (0.125–0.63 mm), poorly sorted to unsorted, with 50–100% carbonate in pore space and, in addition, several per cent of clay cement. At the same time, due to heterogeneity, the rock properties could vary at different depths even in one geological structure (e.g. in E6) (Shogenov et al. 2013b).

The main difference between previous classifications, given for hydrocarbon reservoirs, recommendations for reservoirs 'appropriate'/'not appropriate' for CGS and the new classification proposed in this research for the sandstones of the Deimena Formation is the overlapping porosity of rock groups divided by permeability (Table 1). For this reason every group is subdivided into classes distinguished by porosity. Still, the petrophysical parameters depending on porosity, like bulk density and velocity, can also overlap for some classes. However, every reservoir quality rock class is characterized by a unique set of petrophysical, chemical, mineralogical and microstructural parameters (Table 2, Figs 4, 6–8).

The initial and altered effective porosity and permeability of the reservoir samples from the E6 structure were ranked as of 'high-1' and 'good' reservoir quality (classes I and III, respectively), or 'very appropriate' and 'appropriate' for CGS, respectively (groups 1 and 2, Table 1). The porosity and permeability of sandstones from the E7 structure were significantly lower (class VI) than in rocks from E6. The initial and altered permeability of the clay-cemented sandstones from the E7 structure (0.13–0.18 mD) and the initial permeability of the carbonate-cemented sandstones from the South Kandava structure (0.001–0.28 mD) were in 'very low' reservoir quality class VIII. The reservoir quality of rocks decreases with increasing depth because of rock compaction, rising temperature, conformation of grains and increasing quartz cementation of sandstone with growing depth in the Baltic Basin (Shogenova et al. 2001a, 2001b, 2009a; Sliaupa et al. 2001). Our study confirms these results – the shallowest offshore structure E6 has the best reservoir properties of sandstones.

The effective porosity of most samples did not change during treatment and was supported by stable (E7-1, E7-5) or little varying (E7-4, E7-6) permeability values (Table 4, Fig. 2). Other samples showed some variation in effective porosity with stable permeability. At the same time, sample E7-3 revealed a slight decrease in effective porosity but a significant increase in permeability (up to 2 times after the alteration experiment). An increase in permeability, correlated with a decrease in grain density and supported by unchanged initial porosity, could be explained by modifications of pore space geometry and grain shape changes that control capillary forces (Schön 1996). We determined a minor dissolution of sandstone cement, including dolomite and ankerite (Table 3, Fig. 6), which was insignificant for effective porosity change but substantial for permeability increase. Mineral precipitation and/or cement dissolution, as well as relocation and displacement of clay cement, which blocks pores, took place in the samples characterized by decreased effective porosity. Thin section study showed that the clay fraction, represented by an insignificant amount (about 5%) of kaolinite and/or illite in porous media of the studied samples, was displaced from the pores after the alteration experiment (Figs 4, 6, 7). The type of clay mineral present is important for the reservoir quality of sandstone. Different influence of kaolinite and illite on porosity and permeability change has been explained earlier. According to Tucker (2001), pore-filling kaolinite reduces the porosity of sandstone, but has little effect on permeability, while pore-lining illite reduces permeability considerably by blocking pore throats but has little effect on porosity. We are not focusing on the clay fraction due to the minor presence of clay minerals in the studied samples and insignificant alteration of properties related to the clay cement displacement after the experiment.

Before the alteration experiment trans-res carbonate-cemented quartz sandstone samples Kn24-4 (ankerite-cemented) and Kn27-4 (calcite-cemented) had low and very low effective porosity and permeability (class VIII, Tables 1, 4). In both samples we determined the dissolution of ankerite and calcite cements with minor displacement of clay cement blocking pores. However, both types of cement dissolution affected the alteration of petrophysical properties. We observed a more significant increase in effective porosity and permeability in calcite-cemented sandstone Kn27-4. The sample was relocated from the 'very low' reservoir quality class VIII rank ('not appropriate' for CGS) to 'high-2' quality class II ('very appropriate' for CGS) due to final improvement in petrophysical properties (Tables 1, 4). These changes were supported by the dissolution of the carbonate mineral phase, expressed in the decrease in CaO values (3.5%) measured by XRF analysis after the alteration experiment (Table 3). The dissolution of the carbonate mineral phase in ankerite-cemented sandstone Kn24-4 is also expressed by the decrease in CaO (1.7%) measured by XRF analysis after the alteration experiment (Table 3). This sample was relocated from 'very low' reservoir quality class VIII ('not appropriate' for CGS) to 'moderate' quality class IV ('appropriate' for CGS) (Tables 1, 4). Minor improvement of the rock properties compared to calcite-cemented sandstone Kn27-4 was observed (Table 4).

Previously reported results of laboratory experiments, numerical modelling and field monitoring of CO_2–reservoir rock interactions (e.g. Czernichowski-Lauriol et al. 2006; Egermann et al. 2006; Izgec et al. 2008; Kaszuba & Janecky 2009; Bemer & Lombard 2010; Nguyen et al. 2013) concur with our data. Partial dissolution of carbonate cement (calcite, dolomite and ankerite) and other secondary minerals associated with significant increase, and in some places slight variation in porosity and permeability were determined in the reservoir rocks.

Thin section study allowed qualitative estimation of the mineral dissolution in carbonate cement. Although we expected carbonate cement to dissolve more intensely, it dissolved only on the edges of grains and partially inside the pore filling. This phenomenon could be explained by the reduction in the acidity of brine and increase in pH to the pre-experimental level during the experiment due to the dissolution of a certain amount of carbonate cement material. This means that CGS in the areas with substantial carbonate cementation of reservoir rock will not cause a significant dissolution of cement in the long term, which lowers the level of leakage risks.

However, this statement is very site-specific and must be approved by fluid-flow modelling in every certain storage site.

The grain and bulk dry density and P-wave velocity measured in this research were mainly within the limits corresponding to the data earlier reported for the middle part of the Baltic Cambrian Basin. Maximum values of P-wave velocity measured before the experiment for carbonate-cemented sandstones from the South Kandava structure (5400–4556 m s^{-1}) were similar to the data measured earlier for carbonate-cemented sandstones of the northern shallow part of the basin. The decrease in P-wave and S-wave velocity in the dry samples after the alteration experiment, determined in most of the reservoir sandstones, is explained by the increase in porosity and/or decrease in grain and bulk density (Fig. 5). The lowest acoustic velocity before the alteration was in the range of the lowest previously obtained values (Shogenova et al. 2001a, 2001b), while after the experiment the P-wave velocity of sample E7-6 became the lowest among earlier and recently measured velocities (Table 4). The grain density, measured before the alteration experiment for 12 sandstone samples, was in the limits of 2664–2746 kg m^{-3}, decreasing after the experiment to 2635–2676 kg m^{-3} (Table 4).

The studied samples from the offshore reservoirs (E6 and E7) are typical rocks of the Deimena Formation of Cambrian Series 3 in the Baltic Basin. Thereby, petrophysical alterations described in this study are an important piece of the puzzle when CGS will be modelled in the basin scale.

According to the data in Shogenov et al. (2013a, 2013b) and the classification presented herein, the South Kandava, E6 and E7 structures were re-estimated for CGS in the Cambrian Deimena Formation in the Baltic Basin. The reservoir sandstones of the Deimena Formation in the South Kandava and E6 structures had an identical average porosity of 21%, while their average permeability differed twofold, being 300 and 150 mD, respectively. The estimated good reservoir quality of sandstones in these structures was assessed as ‘appropriate’ for CGS. The reservoir quality of the sandstones of the E7 offshore structure, estimated as ‘cautionary-2’ (average porosity 12% and permeability 40 mD), was the lowest in the studied structures and was assessed as ‘cautionary’ for CGS.

CONCLUSIONS

1. Based on the recently and earlier measured gas permeability and porosity, a classification of the reservoir quality for CO_2 geological storage was proposed for sandstones of the Deimena Formation of Cambrian Series 3 in the middle part of the Baltic Basin. According to their practical application to CGS, the rocks were divided into four groups by permeability (very appropriate, appropriate, cautionary and not appropriate) and eight reservoir quality classes were distinguished within the groups by porosity (high-1 and high-2, good and moderate, cautionary-1 and cautionary-2, low and very low). The proposed classification of the reservoir quality of sandstones helped to estimate the significance of their petrophysical changes caused by geochemical processes during the CO_2 injection-like alteration experiment.
2. The rocks of the initially four reservoir quality classes were studied both before and after the CO_2 injection-like alteration experiment. The greatest changes in the composition and properties of the rocks, caused by geochemical alteration during the experiment, were determined in two carbonate-cemented transitional reservoir sandstones from the uppermost part of the South Kandava onshore reservoir (0.2–0.3 m below cap rock). Partial dissolution of pore filling carbonate cement (ankerite and calcite) and displacement of clay cement, which blocks pores, caused a significant increase in effective porosity, drastic increase in permeability and a decrease in samples’ weight, bulk and grain density and P- and S-wave velocity. As a result of these alterations carbonate-cemented sandstones of initially ‘very low’ reservoir quality (class VIII), ‘not appropriate’ for CGS, acquired an ‘appropriate’ for CGS ‘moderate’ (class IV) or ‘very appropriate’ for CGS ‘high-2’ reservoir quality (class II).
3. Significant increase in effective porosity and permeability after the alteration experiment was detected in calcite-cemented sandstone Kn27-4 compared to ankerite-cemented sandstone Kn24-4. Only partial carbonate cement dissolution occurred on the edges of grains and inside the pore filling in the samples with carbonate cement (e.g. E7-3, Kn24-4 and Kn24-7), which is explained by reduction in the acidity of brine and increase in pH equilibrium during the experiment compared to the pre-experimental state.
4. The composition and properties of clay-cemented sandstone with initially ‘very low’ reservoir quality (class VIII), ‘not appropriate’ for CGS, from the lower part of the offshore E7 structure changed slightly. Its permeability (0.18–0.23 mD) was not improved during the experiment and these rocks remained in the ‘very low’ reservoir quality class.
5. Variation in the properties of sandstones from the middle and upper parts of the E7 structure of initially ‘cautionary-2’ reservoir quality (class VI) did not cause significant changes in their reservoir quality, except for one sample with notably increased perme-

ability, rising its reservoir quality into 'moderate' (class IV), 'appropriate' for CGS.
6. Slight variations in the composition and properties of the 'high-1' reservoir quality sandstones from the E6 offshore structure did not cause significant changes in reservoir quality and they remained in their initial quality classes ('high-1' and 'good' quality classes I and III). These changes were interpreted as insignificant mineral dissolution and some displacement of clay cement from the pore space, which caused slight mechanical weakening and a decrease in the weight, grain and bulk density, possible slight increase in the effective porosity in all the structure, as well as probable increase in the permeability of the rocks from the lowermost part of the E6 reservoir.
7. The reservoir sandstones of the Deimena Formation in the South Kandava and E6 structures had an identical average porosity of 21%, but their average permeability differed twofold, being 300 and 150 mD, respectively. The good reservoir quality of sandstones in these structures was assessed as 'appropriate' for CGS. The reservoir quality of the sandstones of the E7 offshore structure, estimated as 'cautionary-2' (average porosity 12% and permeability 40 mD), was the lowest in the studied structures and was assessed as 'cautionary' for CGS.
8. The obtained results indicate some possible physical processes that could occur during CGS in the studied onshore and offshore structures. These results, being the first of this type in the central part of the Baltic Basin, are also important for the southern and western parts of the Baltic sedimentary basin, which have CO_2 storage capacity in the Cambrian aquifer (Lithuania, Sweden, Kaliningrad Region and offshore Poland). However, they should be supported by additional laboratory experiments and fluid-flow modelling of the CO_2 storage in the Cambrian sandstones both in the structures and basin scale for better assessment of the possible storage scenarios and their safety.

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Kambriumi liivakivide reservuaarikvaliteet ja petrofüüsikalised omadused ning nende evolutsioon Balti basseinis CO_2 geoloogilise ladustamise eksperimentaalse modelleerimise vältel

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Käesoleva uurimistöö eesmärkideks olid: 1) anda ülevaade kehtivatest soovitustest ladustamisreservuaaridele ja välja pakkuda nende kvaliteediklassifikatsioon, kasutades Kambriumi Seeria 3 Deimena ladestu katseandmeid; 2) kindlaks teha võimaliku CO_2 geoloogilise ladustamise (CGS) mõju Deimena ladestu liivakivide omadustele ja reservuaari-kvaliteedile; 3) rakendada ettepandud klassifikatsiooni ladustamisreservuaaridele ja nende evolutsioonile CGS-i kestel Balti basseinis.

Baseerudes gaasiläbilaskevõimele ja poorsusele, pakuti välja reservuaarikivimite CGS-i kvaliteedi uus klassifikatsioon Balti settebasseini Deimena ladestu liivakividele, mis on kaetud Alam-Ordoviitsiumi savi- ning karbonaatsete kattekivimitega. Liivakivid jagati läbilaskevõime alusel nelja gruppi vastavalt nende CGS-i praktilisele kasutatavusele ('väga sobivad', 'sobivad', 'ettevaatust nõudvad' ja 'ebasobivad') ning täiendavalt jagati grupid poorsuse alusel kaheksaks reservuaarikvaliteediklassiks.

Mandrilise Lõuna-Kandava ja mereliste E6 struktuuri (Lätis) ning E7 struktuuri (Leedus) petrofüüsikalised, geokeemilised ja mineraloogilised parameetrid määrati enne ning pärast CO_2 sisestamist imiteerivat muutmiseksperimenti. Kõige märkimisväärsemad muutused uuritud kivimite koostises ja omadustes leiti Lõuna-Kandava mandrilise struktuuri ülemiste kihtide karbonaatse tsemendiga liivakivides. Uuritud proovide poore täitva karbonaatse tsemendi (ankeriit ja kaltsiit) osaline lahustumine ning poore blokeeriva savitsemendi eemaletõrjumine põhjustasid nende efektiivse poorsuse märkimisväärse suurenemise, läbilaskevõime drastilise suurenemise ja tera- ning massitiheduse, P- ja S-laine kiiruse ning kuivproovide massi vähenemise. Nende muutuste tulemusel omandasid karbonaatse tsemendiga liivakivid, mis olid algselt 'väga madala' reservuaarikvaliteediga (klass VIII) ja CGS-iks 'ebasobivad', nüüd CGS-iks 'sobiva' 'keskpärase' kvaliteediklassi (klass IV) või CGS-iks 'väga sobiva' 'kõrge-2' kvaliteediklassi (klass II). 'Väga madala' (klass VIII) kvaliteediklassiga reservuaari savitsemendiga liivakivide läbilaskevõime ei paranenud. Muutmiskatsed, mis tehti uuritud mereliste puhaste kvartsliivakividega E6 ja E7 struktuuridest, põhjustasid nende kivimite omadustes vaid tähtsusetuid muutusi. Nende liivakivide algsed reservuaarikvaliteedi näitajad ('kõrge-1' ja 'hea' ning klassid I ja III E6-s ning 'ettevaatust nõudvad-2' ja klass VI E7-s) peamiselt säilisid.

Lõuna-Kandava Deimena ladestu struktuuri reservuaari liivakivid keskmise poorsusega 21% on poorsuse poolest identsed kivimitega E6 struktuurist, kuid neil on kaks korda suurem läbilaskevõime: vastavalt 300 ja 150 mD. Hinnanguline hea liivakivide reservuaarikvaliteet nendes struktuurides hinnati CGS-iks 'sobivaks'. E7 merelise struktuuri liivakivide reservuaarikvaliteet, mis oli hinnanguliselt 'ettevaatust nõudev-2' (keskmine poorsus 12% ja läbilaskevõime 40 mD), oli uuritud struktuuridest madalaim ning hinnati kui CGS-iks 'ettevaatust nõudev'.

Esmakordselt uuriti laboratoorselt simuleeritud CGS-ile allutatud liivakivide petrofüüsikalist evolutsiooni. Saadud tulemused on olulised, mõistmaks füüsikalisi protsesse, mis võivad toimuda CO_2 ladustamisel Baltikumi mandrilistes ja merelistes struktuurides.