

Ferroan dolomite cement in Cambrian sandstones: burial history and hydrocarbon generation of the Baltic sedimentary basin

SAULIUS SLIAUPA^{1,2}, JOLANTA CYZIENE³, NICOLAAS MOLENAAR⁴ & DALIA MUSTEIKYTE³

¹ Institute of Geology and Geography Lithuania, Department of Regional Geology, T. Sevcenkos 13, LT-2600 Vilnius, Lithuania. E-mail: sliaupa@geo.lt

² Vilnius University, Department of Geology and Mineralogy, M.K.Ciurlionio 21/27, LT-03101 Vilnius, Lithuania.

³ Lithuanian Geological Survey, S.Konarskio 35, LT-03123 Vilnius, Lithuania. E-mail: jolanta.ciziene@lgt.lt

⁴ Institute of Environment & Resources, Technical University of Denmark, Bygningstorvet, Building 115, DK-2800 Kgs. Lyngby, Denmark. E-mail: nim@er.dtu.dk

ABSTRACT:

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The conditions and timing of carbonate cementation in Cambrian sandstones of the Baltic sedimentary basin were determined by oxygen and carbon stable isotope and chemical data in combination with optical and cathodoluminescence petrographic studies. Studied samples represent a range in present burial depth from 340 to 2150 m. The carbonate cement is dominantly ferroan dolomite that occurs as dispersed patches of poikilotopic crystals. Temperatures of dolomite precipitation, based on $\delta^{18}\text{O}$ values, range from 27°C in the shallow buried to 95°C in the deep buried sandstones. The burial history modelling points to development of most of the dolomite cement during rapid Silurian-Devonian subsidence and Carboniferous-early Permian uplift. A wide range of precipitation temperatures indicate that temperature was not a major factor in triggering the carbonate cementation. Dolomite precipitation is related to early stages of organic matter maturation and thus to the oil generation history in the basin. $\delta^{13}\text{C}$ values vary from +0.03‰ to -6.2‰ (PDB), suggesting limited addition of carbon from an organic source, with the major part derived from marine bicarbonate. The sourcing of carbon from the organic-rich Cambrian shales is identified from the distribution of $\delta^{13}\text{C}$ values in the dolomite cement within the Cambrian section. The chemical composition of the dolomite cement shows a depth-controlled trend that is coincident with the present-day hydrochemical zonation of the Cambrian aquifer. The increase in the Fe content of the dolomite towards the deeper buried part of the Baltic basin is related to increasing sourcing of ions (Fe and Mg) from adjacent shales.

Key words: Ferroan dolomite cement, Stable isotopes, Cambrian sandstones, Baltic basin.

INTRODUCTION

Carbonate cements are common in siliciclastic sandstones, ranging from pervasive to disseminated cement, with a consequent different influence on

petrophysical properties (KANTOROWICZ & *al.* 1987; BJØRKUM & WALDERHAUG 1990). Dispersed dolomite and ankerite cements are common but minor cements in many hydrocarbon-bearing sandstones (e.g. SMITH 1992, HENDRY & *al.* 2000b). The character of carbon-

ate cements, i.e., their distribution, and mineralogical and chemical composition, can supply information on the chemical conditions during diagenesis and the chemical composition and flow patterns of diagenetic fluids in the sedimentary basin.

Cambrian strata represent the basal part of the Baltic basin succession overlying the western periphery of the East European Craton. The burial depth of the Cambrian deposits changes from surface outcrops in the north of Estonia, to a depth of a few hundred metres in southeast Lithuania, to more than 3 km depth in the western Baltic Sea and north Poland (Text-fig. 1). Consequently, the 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 increasing clay mineral maturity with increasing depth, variations in the sandstone cement composition, with authigenic quartz prevailing in the deep part of the basin and increasingly important carbonate cements in the basin periphery, changes in the pore-water composition, grading from Ca-CO₃ type in the east to Na-Cl type in the west, etc. The carbonate cement of the sandstones ranges in mineralogy from common ferroan dolomite and ankerite to less common calcite and siderite.

The chemical composition of the carbonate cements in the Cambrian sandstones was studied, since this reflects the major trends in the chemistry of the formation palaeowater across the basin resulting from the various water-rock interactions. The precipitation of the dolomite cement marks important changes in the basin evolution and may be attributed to different parameters, including temperature, maturation of the organic matter and clay minerals and influx of mete-

oric water. Oxygen stable isotope values of the carbonate minerals were measured to assess the thermal conditions during precipitation, while carbon stable isotope values were used to trace the carbon sources. The results of these investigations, together with modelling of burial and hydrocarbon generation, allow dating of the dolomite formation. Petrographic studies were carried out to identify different stages in the carbonate cementation.

CAMBRIAN LITHOLOGY

The thickness of the Cambrian succession varies from a few dozen metres in the east to 170 m in western Lithuania (JANKAUSKAS & LENDZION 1992). Sandstones dominate the eastern facies of the Lower Cambrian and grade into shales and siltstones in the west. The Middle Cambrian sandstones, comprising the main oil reservoir, up to 70 m thick, rest on Lower Cambrian shales in western and central Lithuania (Text-fig. 2). The sandstones are fine-grained, well sorted, massive and thick- to thin-laminated and consist mainly of quartz (95-99%) with a minor content of K-feldspar. The sandstone porosity is 20-25% in the shallow eastern part of the basin and decreases to 15-20% in central Lithuania, and up to 3-10% in western Lithuania (SLIAUPA & *al.* 2001). This trend is mainly the result of progressive quartz cementation.

Siltstones are abundant in the Lower Cambrian succession. Mudrocks dominate the western facies of the Lower Cambrian, and are also present as millimetre- to metre-thick layers in the Middle Cambrian sandstones. Illite is the dominant clay mineral, with kaolinite subordinate (LASKOVA 1979), pointing to the

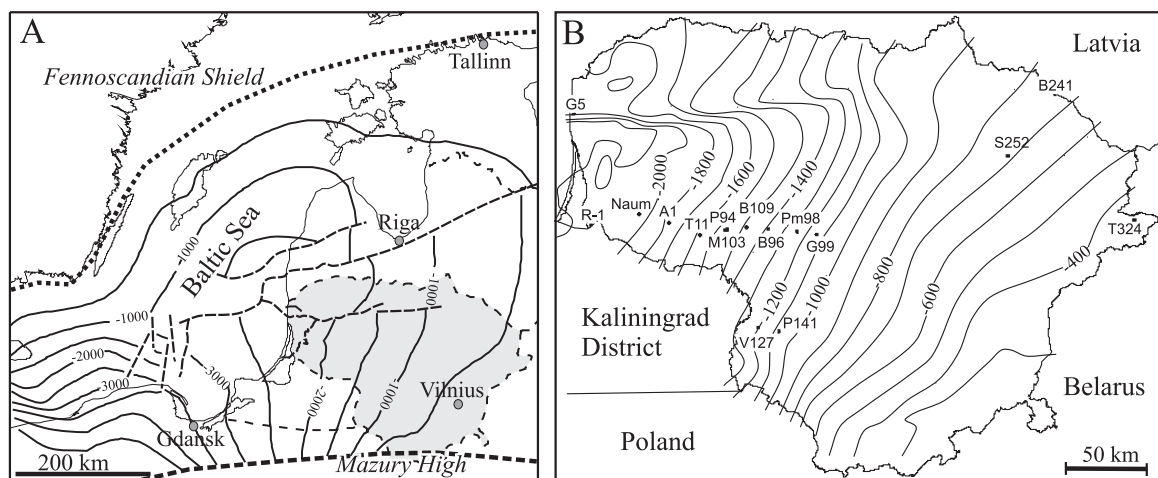


Fig. 1. A – depths (m) of the base of the Cambrian succession in the Baltic basin. B – depths (m) of the top of the Cambrian succession in Lithuania. The locations of studied wells are indicated

high mineralogical maturity of the clays (KIRSIMAE 1999). The mudrocks contain up to 0.2-1% organic matter (KADUNIENE 1979). Together with Ordovician and Silurian organic-rich shales they represent the oil-generating source rocks in the region.

METHODS AND DATA

More than 300 samples were studied by polished thin-section petrography (Nikon MB-21). All thin sections were investigated by standard polarized light and a selection by cathodoluminescence microscopy (CL), with a cold luminoscope (TECHNOSYN) attached to a standard polarized light microscope equipped with a digital camera. Standard operating conditions for cathodoluminescence petrography were 12-15 kV accelerating voltage and 200-600 μ A beam current. Cathodoluminescence microscopy served to identify quartz cement unequivocally and establish textural relationships between detrital and authigenic components and pores. Scanning electron microscopy (SEM) augmented with CL imaging (SEM-CL) helped to confirm the cold luminoscope observations and to visualize cement zonation with back-scattered electron imaging (BEI).

An electron microprobe (Jeol JXA-8200 Superprobe; wavelength dispersive spectrometry) (N=56) was used to determine the Ca, Mg, Fe, Mn and Sr contents of the carbonate cement of 13 Cambrian sandstone samples. The samples were selected from 10 wells representing eastern, central and western Lithuania.

Powder X-ray diffractometry was used to identify the gross mineralogy of the carbonate cement and other components of the Cambrian sandstones.

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values through standard phosphoric acid CO_2 extraction from carbonate cements (13 samples, 9 wells) were measured with an isoprime mass spectrometer and are denoted in ‰ (per mil) deviation

from PDB (PeeDee Belemnite) and SMOW (Standard Mean Ocean Water) standards. The samples were measured against the laboratory standard LEO (Carrara marble) which has been calibrated against the V-PDB carbonate standard (Vienna PDB, also a marble). Measurements were performed on a Micromass IsoPrime continuous flow mass spectrometer supplied with a MultiPrep automated carbonate preparation system. 10 standards were analysed for each batch of samples (50 samples). Concentrated phosphoric acid was added manually. Reproducibility measured as standard deviation for 10 standards is better than ± 0.1 ‰ for carbon and ± 0.2 ‰ for oxygen.

Data of the chemical compositions of Cambrian formation water from 298 wells were available from industrial reports.

CEMENTS IN CAMBRIAN SANDSTONES

Quartz cement predominates in the central and western parts of the basin, occurring at depths greater than 1 km. In central Lithuania the authigenic quartz amounts to 10-15% and increases markedly to 20-30% in western Lithuania. This sharp transition coincides with the 60-70°C isotherm, which can be considered as the major threshold in quartz cementation (WALDERHAUG 1994). The quartz cement formed during the late diagenetic stage (LASKOVA 1978; SIKORSKA & PACZESNA 1997). The intergranular volume is in the range of 26-33%; this is in agreement with the intermediate deep burial conditions during quartz cementation (PAXTON & *al.* 2002).

The carbonate cement shows the opposite trend to the quartz cementation: it is more abundant on the shallow flanks of the basin and decreases in abundance with increasing depth (SLIAUPA & *al.* 2001).

XRD and petrographic examinations indicate that the carbonate cements in the Cambrian sandstones are predominantly ferroan dolomite, calcite and, more

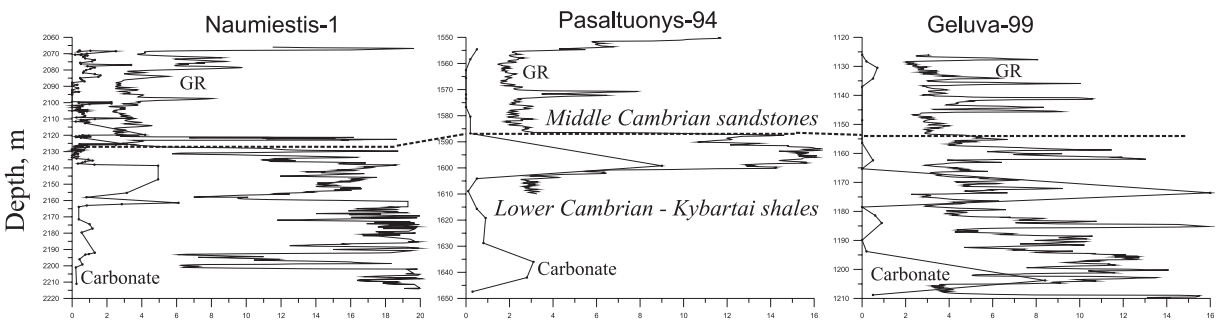


Fig. 2. Comparison of the distribution of carbonate cement (%) and shales (gamma-ray, mkr/h) in the Cambrian succession of wells Naumiestis-1, Pasaltuonys-94, Geluva-99 (see Text-fig. 1 for well locations)

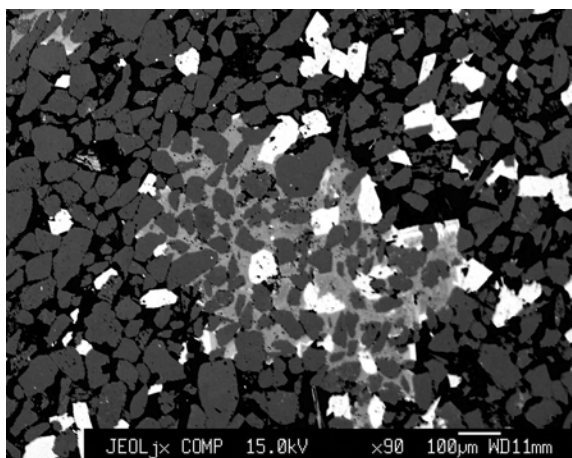


Fig. 3. BSE micro-photographs. A patch of ferroan dolomite (light grey) cementing a number of quartz grains (dark grey) and some K-feldspar grains (bright grains) in the shallow buried Cambrian subarkosic quartz arenite. K-feldspar grains (bright grains; quartz grains are darker grey) have well-developed euhedral authigenic K-feldspar overgrowths. This indicates that the dolomite cement precipitated later than the K-feldspar overgrowths

rarely, siderite. Ferroan dolomite and ankerite are also present in the mudrocks. Ankerite is reported as a common cement in the more deeply buried westernmost part of the Baltic basin in northern Poland (SCHLEICHER 1994).

The carbonate cements show predominantly a dispersed distribution in patches that reach up to 4 cm in diameter in the east and are only of millimetre-scale in the western deeper part of the basin. Patches of ferroan dolomite consist of poikilotopic crystals dispersed throughout the sandstones (Text-fig. 3), thereby cementing a number of detrital sand grains. Individual crystals or small clusters of dolomite crystals up to

tens of microns in size also occur. The calcite cement forms patches up to 5 mm in diameter.

DISTRIBUTION OF CARBONATE CEMENT

The average content of the carbonate cement in eastern Lithuania is about 5% and this decreases in the central part of the basin where it comprises 1.0-1.5% of the rock volume, though some anomalous high values exceeding 5% are also present (Text-fig. 4). The carbonate content is somewhat lower in central Lithuania (Text-fig. 4).

There are some differences in the carbonate distribution in the succession. The average carbonate content in the Middle Cambrian sandstones varies commonly from 0.5% to 1.5% and is about 0.5-1% lower than in sandstones within the Lower Cambrian shaly succession (Text-fig. 2). Furthermore, anomalously cemented sandstone layers containing up to 22% of carbonate occur in the Lower Cambrian and Kybartai shaly packages. The Middle Cambrian sandstone reservoir contains laminae and thin layers of shale, the proportions of which change across the section. Here a direct correlation between the shale and carbonate contents is recognised (Text-fig. 2). Moreover, the high carbonate-content anomalies are spatially confined to the contacts of sandstone and shale layers.

A favourable influence of the carbonate cement on the reservoir quality is stressed by some authors, relating to inhibition of quartz cementation in carbonate-cemented sandstones and the development of secondary porosity induced by dissolution of carbonate cements (KILDA 2002; KILDA & FRIIS 2002). A small increase in porosity through carbonate cement

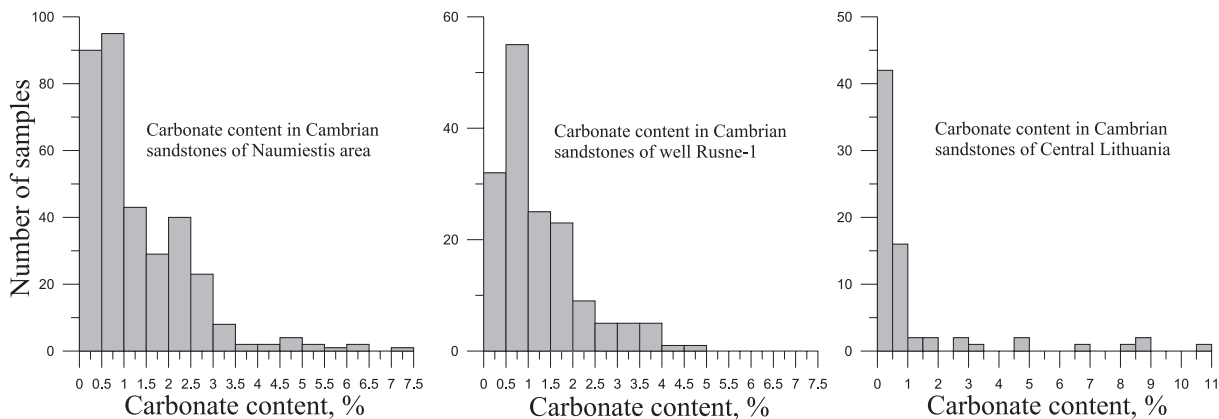


Fig. 4. Histograms showing carbonate content in Cambrian sandstones of Naumiestis area (wells Naumiestis-1, 2, 3, 4), well Rusne-1, and central Lithuania (wells Geluva-99, Milaiciai-103, Pamituvys-98, Pramedziuva-97, Bliudziai-96, Pasaltuonyus-94)

dissolution would indeed be significant in view of the low background porosity (6-7%) of the Cambrian sandstones in western Lithuania. However, carbonate cement content is in most cases reversely correlated to porosity (Text-fig. 5).

RESULTS

Petrography of ferroan dolomite cement

Dolomite cement is non-luminescent. Early and late stage cements can be distinguished, referred to respectively as stages D1 and D2 (Text-figs 6A, B). The early generation dolomite D1 crystals often have more fluid inclusions, whereas the late phase of D2 dolomite overgrowths show zonation in Fe content. The chemical zonation points to gradual growth of the last phase of dolomite under slightly varying conditions. The late dolomite D2 grew syntaxially on the dolomite D1 (Text-fig. 6A, B).

Some of the pores filled by dolomite are oversized and thus are considered as the secondary pores. These oversized pores locally contain quartz inclusions (Text-fig. 7), indicating dissolution and replacement of detrital grains.

Calcite cement seems to be relatively early (i.e. pre-compaction), and beds with pervasive calcite cement have no quartz cement. However, this occurs in the shallow buried parts of the basin where quartz cement anyway is uncommon.

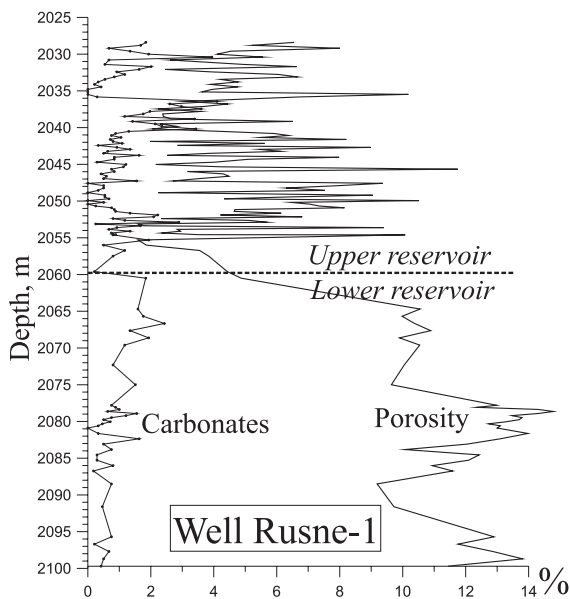


Fig. 5. Comparison of carbonate cement content and porosity of Cambrian sandstones, well Rusne-1

It is difficult to estimate the relative timing of dolomite precipitation from intergranular pore volumes (IGV) because the dolomite often occurs in and around seemingly oversized pores. In some cases, quartz inclusions or outlines of former possible carbonate grains suggest that the dolomite is in part replacing detrital grains. Detrital feldspar grains have fully developed, euhedral overgrowths in the dolomite-cemented patches (Text-fig. 3). Feldspar overgrowths developed during early diagenesis, clearly before dolomite and quartz cement precipitation started. However, there are several different textural relationships between quartz cement and dolomite. The quartz grains in the central parts of larger poikilotopic dolomite patches have only thin and discontinuous overgrowths, denoting an early

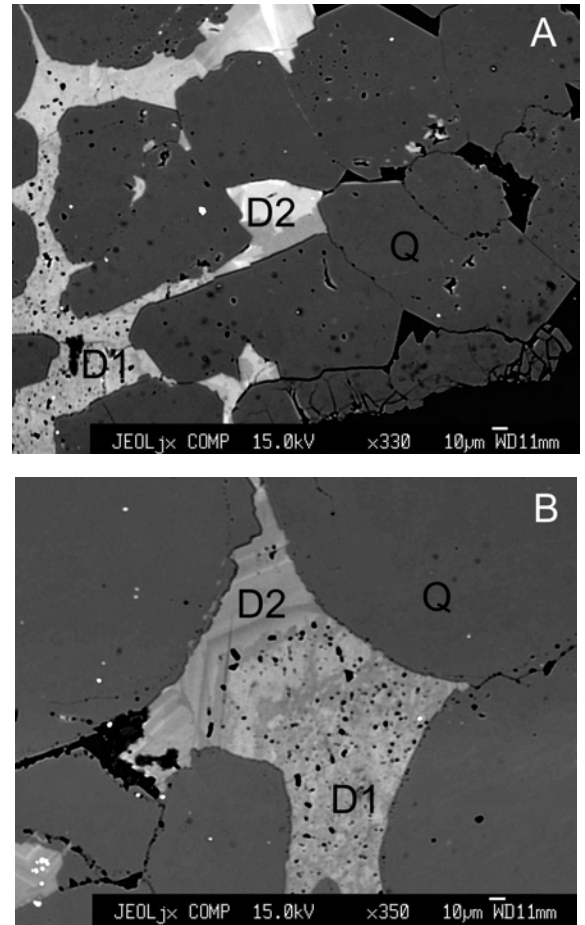


Fig. 6. BSE micro-photographs. Quartz (Q) sandstone cemented by dolomite. The outer parts of the dolomite (D2) cement show more Fe-zonation. A-well Taurage-11, depth 1733.4 m, B-well Pamituvys-98, depth 1262.4 m. Note that the older D1 is in contact with detrital quartz grains with thin, incipient quartz overgrowths, whereas the outer fringes are cementing quartz detrital grains with thicker, more developed quartz overgrowths

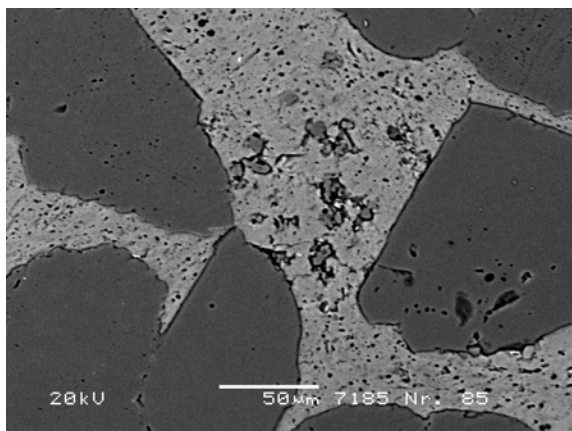


Fig. 7. CL microphotograph of dolomite cement. Some quartz inclusions in the central part of the dolomite cement and the oversized nature suggest replacement of a lithic detrital grain

stage of quartz overgrowth development (Text-fig. 6b). The amount of quartz cement increases in the outer margins of the dolomite-cemented patches. Smaller dolomite crystals occur in pores filled mainly with quartz cement, suggesting dolomite precipitation during a later stage of quartz cementation. Dolomite precipitation is thus synchronous with quartz cement precipitation, and started at a very early stage or just before quartz cementation started. Quartz cementation took place mainly during rapid Silurian-Devonian burial of the Cambrian succession (MOLENAAR & *al.* 2007). It appears therefore that the carbonate cement grew over a certain period of time concurrently with quartz cement precipitation.

Chemical composition of the ferroan dolomite cement

The chemical composition of the ferroan dolomite is rather variable (Table 1). However, it does form a common trend, as illustrated in the triangular plot of CaCO_3 , MgCO_3 and FeCO_3 % (Text-fig. 8). FeCO_3 increases at the expense of the MgCO_3 . CaCO_3 % also shows minor decrease with increasing FeCO_3 %. MnCO_3 content averages 1.04% (σ 0.5997). The SrCO_3 content is low, with an average of 0.017% (σ 0.0191%). Both Mn/Ca and Sr/Ca show random variation with depth. The FeCO_3 content in the dolomite changes from 4.34% to 17.56% (Text-fig. 9). FeCO_3 contents vary up to 5% within a particular sample. The correlation coefficient between FeCO_3 and MgCO_3 is as high as -0.95; the linear trend is described by the first-order correlation equation $\text{MgCO}_3 = -1.4 \times \text{FeCO}_3 + 42.1$. The FeCO_3 content increases systematically with burial depth from 4 to 27%, with ferroan

dolomite being replaced finally by ankerite (Text-fig. 9). The easternmost wells (Svedasai-252, Text-fig. 1 for well location) shows anomalous enrichment in iron (average 8%), aberrant from the general iron-depth trend. The sample from the well Rusne-1 is also somewhat anomalous due to a lower iron content. Concurrent with increasing FeCO_3 content, CaCO_3 decreases somewhat, suggesting that some of the Fe is in Ca-lattice positions. There is no discernable difference between the sandstone samples obtained from thick sandstone bodies and from sandstone layers within the shales.

$\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the ferroan dolomite

The oxygen isotopic composition of a carbonate depends primarily on temperature-dependent fractionation and on the oxygen isotopic composition of the water from which the carbonate precipitated (MILLIKEN & *al.* 1981; HOEFS 1987; LONGSTAFFE 1987; SAIGAL 1987; BEUKES & *al.* 1990; MAHON & *al.* 1998; WORDEN & *al.* 1999). The carbonate-water $\delta^{18}\text{O}$ equilibrium may be evaluated for carbonate at any given temperature by the experimental fractionation equations for dolomite (LAND 1983) and ankerite (DUTTON & LAND 1985). The carbon isotope composition is related to the balance of inorganic and organic sources and the processes involved, which control the carbon isotopic composition of the CO_2 reservoir. The carbon stable isotope composition reflects the source of CO_2 for precipitation, such as meteoric or seawater, marine

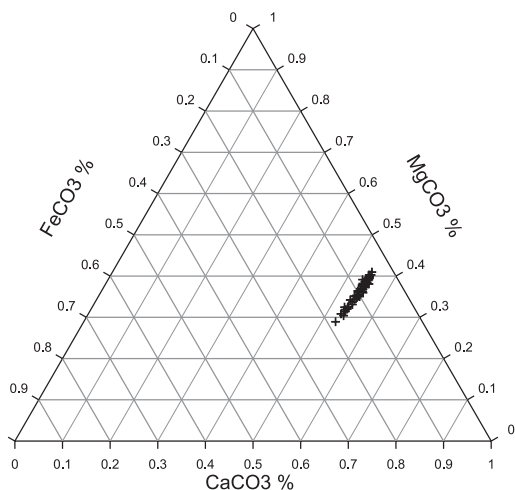


Fig. 8. Triangular plot of CaCO_3 , MgCO_3 and FeCO_3 compositions of ferroan dolomite cement of Cambrian sandstones (Lithuania). The increase in FeCO_3 content takes place at the expense of MgCO_3 content. The relatively minor decrease in CaCO_3 % with increasing FeCO_3 % suggests minor replacement of Ca^{2+} by Fe^{2+}

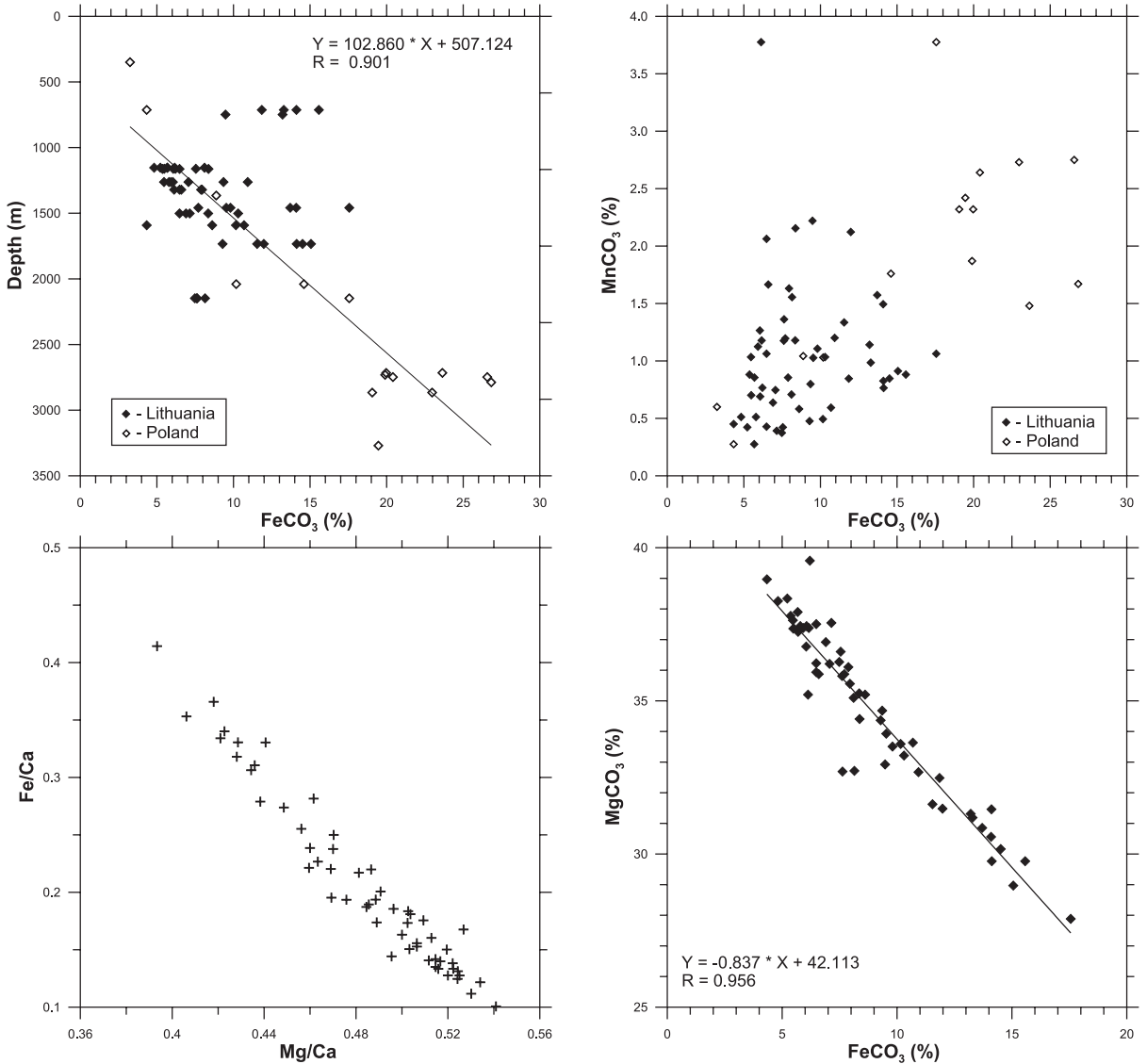


Fig. 9. Chemical composition of ferroan dolomite cement of Cambrian sandstones of Lithuania (filled symbols). For comparison, dolomite and ankerite cements of the Polish part of the basin are also shown (open symbols) (after SCHLEICHER 1994)

carbonate shell dissolution, or various biochemical processes including microbial oxidation of organic matter, methanogenesis and fermentation (ALLEN & MATTHEWS 1982; LAND 1983; LOHMANN 1988).

$\delta^{18}\text{O}$ (PDB) values of the carbonate cement show a distinct depth-controlled trend, decreasing from -5.0/-6.2‰ (SMOW 25.7-24.6‰) in eastern Lithuania and -6.8/-11.3‰ (SMOW 23.9-19.2‰) in central Lithuania, to -11.7/-14.3‰ (SMOW 18.9-16.2‰) in the west (Table 2). The correlation coefficient is -0.89 (Text-fig. 10).

Contrasting with the oxygen isotope compositions, the carbon isotope compositions do not show any dis-

tinct depth trend (Table 2). $\delta^{13}\text{C}$ (PDB) values range from +0.03‰ in the well Aukstupiai-1 to -6.2‰ in the well Rusne-1 (Text-fig.10), which are both representative of the central part of the Baltic basin. There is, however, a clear difference between samples collected from thick sandstone bodies and thinner sandstone layers in the shaly Lower Cambrian succession. $\delta^{13}\text{C}$ (PDB) values are heavier than -2‰ in the thick sandstone bodies, and more negative than -2‰ in sandstones in the shaly part of the Cambrian section. It is noticeable that for the dolomite cement of the latter group there is a more negative trend in $\delta^{13}\text{C}$ values with increasing depth (Text-fig. 10).

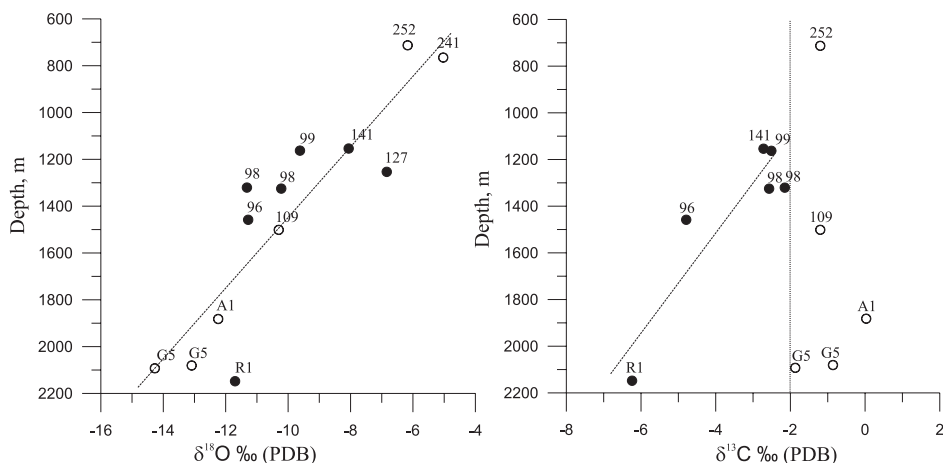


Fig. 10. $\delta^{18}\text{O}$ vs. depth and $\delta^{13}\text{C}$ vs. depth of ferroan dolomite cement of Cambrian sandstones. Open dots indicate samples from thick sandstone bodies, black dots show samples of sandstones intercalated with shales. Well numbers are shown

DISCUSSION

Formation water and dolomite cementation

The calcite cement seems to be restricted to shallow parts of the basin, and is gradually substituted by ferroan dolomite and ankerite in the more deeply buried successions. The carbonate cement mineralogy must be related to the chemistry of the pore fluids which, in the case of the Lithuanian Cambrian sandstones, shows a clear trend of increasing Fe content towards the more deeply buried succession.

The lateral changes in the pattern and chemical composition of the ferroan dolomite are significant, as is the general pattern from calcite to dolomite to ankerite towards the deepest buried Cambrian succession. Such trends can be controlled by pore-water chemistry and framework grain composition, as well as petrophysical properties such as permeability and porosity (e.g., MORAD 1998).

The dolomite cement, in contrast with the calcite cement, is in chemical equilibrium with the present-day Cambrian formation water (MOKRIK 2003). The composition of the formation water varies considerably across the basin. Salinity changes from 1 g/l in eastern Lithuania to 200 g/l in western Lithuania, and this is associated with significant changes in the proportions of the major ions, the pore-water chemistry changing from Ca-HCO₃ type in the east to Na-Cl type in the west.

As was mentioned above, the ferroan dolomite shows a distinct increase in iron content with increasing burial depth. Furthermore, in the deepest part of the basin the ferroan dolomite grades to ankerite (SCHLEICHER 1994) (Text-fig. 9). These changes correlate with changes in the iron content in the Cambrian

formation water. The iron content in the pore water is around 0.8-13 ppm in eastern Lithuania. In particular, Fe⁺² concentration in the well Tverecius-336 is 6.7 ppm, and the content of Fe⁺³ is 4.4 ppm. In western Lithuania, the iron concentration increases to about 55-65 ppm; the formation water of the Cambrian of the well Rusne-1 contains 64 ppm of Fe⁺², with Fe⁺³ below the detection limit. Also, the Mg content increases from around 15-20 g/l in the east to 40 g/l in the west. No influence of proximity to shales on the iron content in the carbonate cement is evident. However, it should be mentioned that evidence of transfer based on elemental data is often inconclusive (cf. MILLIKEN & *al.* 1994).

Changes in the chemical composition of the diagenetic dolomite cement suggest that the basin-scale variations in the composition of the formation water were already distinct in the Palaeozoic Baltic basin during the major stage of carbonate precipitation, and were similar to the present-day trends in Cambrian formation water chemistry.

Since the depositional environment and detrital sandstone composition do not change laterally, the chemical trends in the formation water must be due to diagenetic processes in the adjacent and interbedded shales that are depth (temperature) controlled. Diagenesis in the shales might have influenced the pore-water chemistry in adjacent sandstones. In particular, the smectite-to-illite transformation leads to the release into the pore water of iron and magnesium, and possibly also calcium (BOLES & FRANKS 1979). This may lead to authigenesis in the shales but can also cause transport of released chemical elements into the sandstones, particularly when the shale intervals are relatively thin (WINTSCH & KVALE 1994). The mineral composition of the Cambrian clays underwent con-

siderable transformations in the course of basin subsidence. Even in shallow settings, smectite has been partly to completely transformed into illite, which is attributable to the time factor (KIRSIMAE & *al.* 1999; RAIDLA & *al.* 2006). XRD analyses indicate that the Cambrian clay fraction is dominated by illite with very minor amounts of interlayered smectite-illite in the shallow-buried part of the basin. The rate of Fe supply and Mg from smectite depends on the temperature as well as potassium supply. This would explain the observed change in Fe concentrations in the Cambrian pore fluids, with increasing Fe content with depth.

Sources of carbon

Dolomite and ankerite cements have been described in sandstones as nearly always occurring as disseminated and minor cements. Although some dolomite has been interpreted as early marine diagenetic, taking place before any substantial burial

(HENDRY & *al.* 2000a), most developed during burial diagenesis (SMITH 1992; SCHLEICHER 1994; HENDRY & *al.* 2000b). A rather large variability in chemical compositions has been reported, with mineralogy ranging from dolomite to ankerite, or dolomite with ankerite overgrowths.

Natural waters tend to show a characteristic range of isotope values, which in turn are mimicked by the precipitated carbonates. $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ ratios are indicative of the depositional and diagenetic environments (HUDSON 1977; NELSON & SMITH 1996). They suggest that the dolomite in the Cambrian sandstones precipitated from marine-type water (Text-fig. 11). The carbon isotope composition of the ferroan dolomite cement is slightly enriched in ^{12}C , with an average $\delta^{13}\text{C}$ (PDB) value of -2.4‰ , which is similar to that of the ankerite cement in the westernmost part of the Baltic basin and the ferroan dolomite cement in the adjacent Mazury High, averaging -2.5‰ (SCHLEICHER 1994) (Text-fig. 12). These low negative values suggest that a small amount of carbon was derived from carboxylic acids during thermal cracking of the organic matter in the source rocks.

Comparison with other basins, such as the North Sea, shows a large variation in carbon isotope values (Text-fig. 13). Some of the dolomite and ankerite cements have a distinct contribution of light organic carbon, whereas others show a more marine signature. The carbon source is thus variable and reflects different stages of the basin evolution.

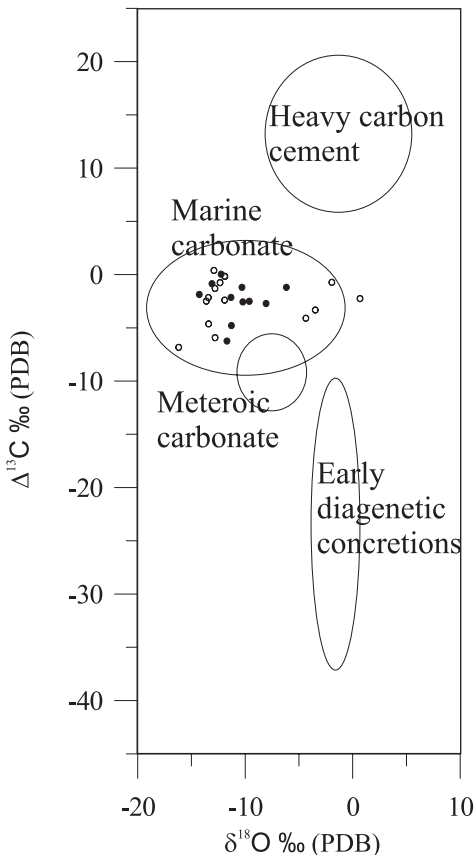


Fig. 11. $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ of ferroan dolomite and ankerite cements of Cambrian sandstones. Filled symbols denote Lithuanian samples, open symbols are samples from the Polish part of the basin (data from Poland are from SCHLEICHER 1994). Environment discrimination fields by HUDSON (1977)

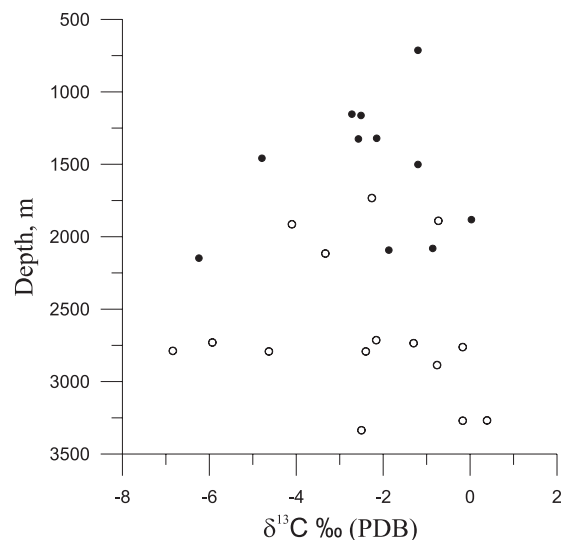


Fig. 12. $\delta^{13}\text{C}$ vs. depth of ferroan dolomite (diamonds) and ankerite cements (squares) of Cambrian sandstones. Filled symbols indicate Lithuanian samples, open symbols are samples from the Polish part of the basin (SCHLEICHER 1994)

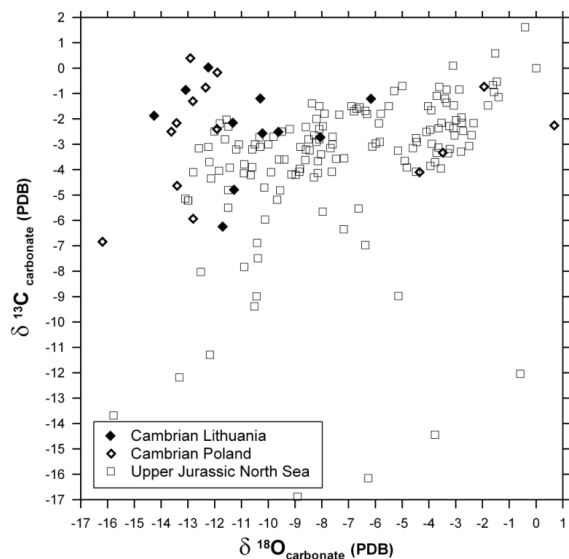


Fig. 13. Comparison of $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ of ferroan dolomite and ankerite cements of Baltic Cambrian sandstones and Upper Jurassic sandstones of the North Sea

The Cambrian, Ordovician and Silurian organic-rich shales of the western half of the Baltic basin are located in the oil window, thus implying an advanced stage of the cracking of the organic matter (BRANGULIS & al. 1993; SCHLEICHER & al. 1993; SLIAUPA & al. 2004). Still, $\delta^{13}\text{C}$ values for the ferroan dolomite and ankerite in the Baltic Cambrian sandstones are somewhat heavier in comparison to those in the major petroleum basins (MACAULAY & al. 2000; STEWART & al. 2000). The decarboxylation of organic acids and kerogen breakdown provided only a limited amount of carbon for the formation of the carbonates in the Cambrian sandstones, and the main source of ions was the marine connate water, and possibly some from dissolved carbonate ma-

terial in the overlying Ordovician carbonaceous-shaly succession. The carbon sourcing from the Cambrian shales is reflected by the difference in the $\delta^{13}\text{C}$ values of the dolomite cement in the thick sandy bodies and in the sandstones within shales, the latter showing generally lighter $\delta^{13}\text{C}$ values. Furthermore, the cracking of the organic matter in the shales increasingly affected the isotope composition of the sandstone cements with increasing burial depth (Text-fig. 10), similarly to the other petroleum basins where a direct impact of shale diagenesis on the carbon isotope composition of the carbonate cement was reported (e.g. BALLENTINE & al. 1996; HASZELDINE & al. 2000; EHRENBERG & al. 2002). The sourcing of other ions (magnesium, iron, calcium) from the shales is evident from the more abundant carbonates in the Cambrian sandstones within shale successions than in the thick sandstone packages. Furthermore, the carbonate cement content in the Middle Cambrian reservoir is higher in the clay-containing laminated sandstones than in the massive sandstones.

Palaeotemperatures and causes of dolomite cementation

The $\delta^{18}\text{O}$ value of the carbonate cement depends primarily on the temperature. The water composition is the other important factor influencing the isotope composition of the diagenetic minerals. As a first approximation, $\delta^{18}\text{O}$ correlates with the present-day temperatures of the Cambrian succession (Text-fig. 14A). The $\delta^{18}\text{O}$ (SMOW) value of the Cambrian formation water of central and western Lithuania, characterised by a stagnant hydrodynamic regime, is -5‰ (MOKRIK 2003). Only in the shallow periphery of the basin, subject to Quaternary influx of the glacial meltwater and

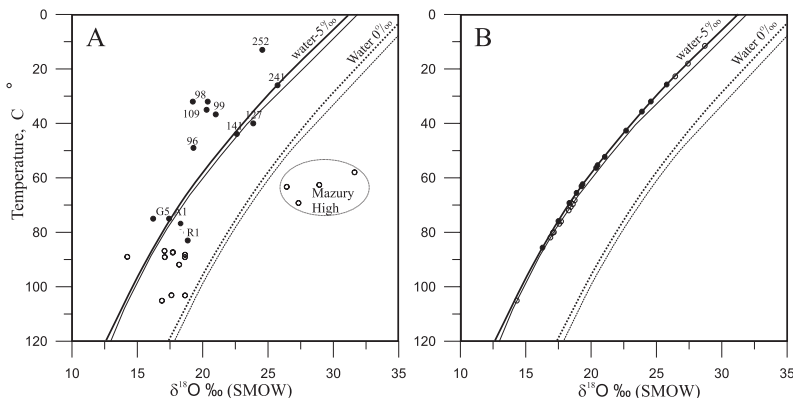


Fig. 14. A- $\delta^{18}\text{O}$ vs. present temperatures and B-reconstructed temperatures of precipitation of dolomite and ankerite cements of Cambrian sandstones assuming pore water composition -5‰ . Black dots denote Lithuanian samples, well numbers are indicated. Open dots show samples from the Polish part of the basin (SCHLEICHER 1994). The water lines calculated after FISHER & LAND (1986) for ankerite equilibrium and LAND (1983) for dolomite equilibrium

meteoric waters, is this value lighter than -10‰. According to LOHMANN & WALKER (1989), sea water during the Cambrian had $\delta^{18}\text{O}$ (SMOW) values about -5‰, or maybe even more negative (VEIZER & *al.* 1997). Accordingly, a value of -5‰ was assumed for reconstructing the thermal regime during the dolomite precipitation (Text-fig. 14B). The dolomite-water oxygen isotope fractionation equation of LAND (1983) was used for this purpose. The reconstructed temperatures of the dolomite cement formation in western Lithuania are in the range of 67-86°C, which is close to the present-day temperatures. The dolomite precipitation temperatures are 40-62°C in central Lithuania, whereas they are 26-31°C in eastern Lithuanian and are often higher by 15-20°C than the present-day temperatures.

The oxygen isotope composition of the ankerite cement of the western periphery of the basin (SCHLEICHER 1994), assuming a $\delta^{18}\text{O}$ (SMOW) value of -5‰ for the formation water, gives precipitation temperatures of 67-82°C that are 20-35°C lower than present-day temperatures (90-100°C). Burial depth and temperature thus increased further after ankerite precipitation. Also, the dolomite cement in the Mazury High shows much lower precipitation temperatures than the present-day ones (Text-fig. 14).

A wide range in precipitation temperatures implies that temperature was not an important factor in triggering dolomite cementation, nor the organic-rich

shales are the main source of carbon (only a small part of the organic carbon in dolomite and ankerite cements is identified from stable isotope composition, as discussed above).

The carbon dioxide and organic acids strongly influence, even in small concentrations, the carbonate equilibrium in the system. The organic acids from organic matter maturation in the shales seem to have been the cause of carbonate mobilization and dolomite precipitation at a certain time determined by organic matter type and maturation rates in the source rocks. In carbonate-poor sandstone, like the Cambrian quartzarenites, the migration distance of such organic acids will be rather large before carbonate reactions buffer the acids, resulting in dispersed distribution of the carbonate cement in sandstones. Due to the closed geochemical system, the amounts of dolomite and ankerite are minor, merely a few percent.

Burial history and timing of cementation

According to existing palaeotectonic reconstructions, Cambrian through early Silurian time was characterised by a low subsidence rate (SLIAUPA & *al.* 1997; POPRAWA & *al.* 2001). The rate of subsidence increased markedly during late Silurian and Devonian times, which accordingly affected the thermal regime

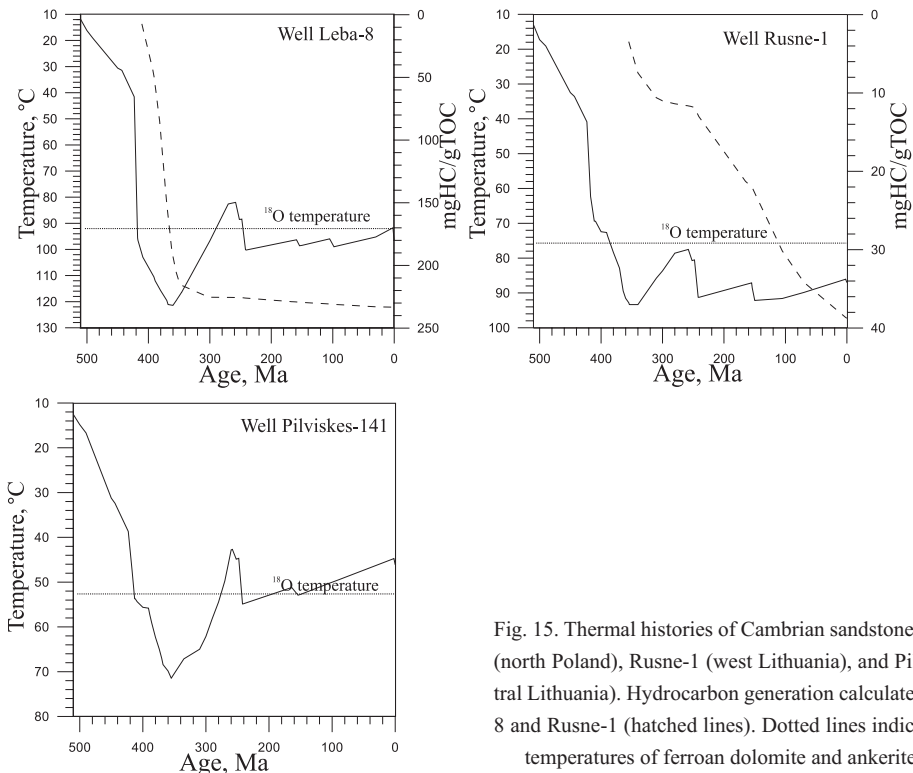


Fig. 15. Thermal histories of Cambrian sandstones of wells Leba-8 (north Poland), Rusne-1 (west Lithuania), and Pilviskes-141 (central Lithuania). Hydrocarbon generation calculated for wells Leba-8 and Rusne-1 (hatched lines). Dotted lines indicate reconstructed temperatures of ferroan dolomite and ankerite precipitation

of the Cambrian deposits (Text-fig. 15). Uplift and erosion took place during the Carboniferous – early Permian, especially the western and eastern periphery of the basin and the Mazury High (MOKRIK 2003). The uplift stage was succeeded by further subsidence during the Mesozoic.

According to the burial modelling, temperatures reconstructed from the oxygen isotope composition of the ankerite were attained (and exceeded) during the late Silurian in the westernmost part of the Baltic basin, whereas this temperature level was reached in Lithuania by the end of the early Devonian and in the Middle Devonian (Text-fig. 15). In northern Poland and central and eastern Lithuania, the Cambrian sandstones were uplifted during the Carboniferous – early Permian uplift event that was followed by the Mesozoic subsidence phase.

Precipitation of dolomite and ankerite can be related to the oil maturation. Hydrocarbons are known to have considerable impact on the diagenetic evolution of sandstones (HAWKINS 1978). Oil and gas generation is associated with a release of organic acids that inhibit carbonate cementation and favour quartz precipitation instead (FRANKS & FORESTER 1984). The carbon dioxide and organic acids will influence the carbonate equilibrium in the pore fluids in the sandstones and may induce feldspar dissolution and the generation of secondary porosity.

According to the burial modelling, the generation of hydrocarbons started in the Late Silurian in the westernmost part of the basin and progressed to the east in the Devonian (Text-fig. 15). The uplift event resulted in the termination and slowing down of hydrocarbon generation in the western and central parts of the basin during Carboniferous to early Permian time (Text-fig. 15). The onset of the hydrocarbon generation can be attributed to the generation of the early-stage dolomite and ankerite, whereas the interruption of hydrocarbon generation during the latest Palaeozoic may have resulted in precipitation of the late-stage dolomite. The latter stage is essentially distinct in the Mazury High where, according to the $\delta^{18}\text{O}$ data, the dolomite cementation of the Cambrian sandstones took place at shallow depths during the latest Palaeozoic uplift.

CONCLUSIONS

Calcite, dolomite and ankerite are common but minor cements in Cambrian quartzose sandstones. The literature shows that there is a large range in chemical and isotopic compositions, and in the temperatures of

cement precipitation. In the Cambrian of the Baltic basin in particular, ferroan dolomite predominates, grading into ankerite in the deeper parts of the basin. Oxygen isotope composition indicates that temperature is not directly a factor in dolomite precipitation. Also carbon isotope composition suggests domination of the marine bicarbonate from connate seawater with a variable (though minor) addition of isotopically light carbon from an organic source so that the latter cannot be a direct cause for dolomite (ankerite) formation either. The main factor that triggered carbonate precipitation was probably the generation of hydrocarbons in the basin, which was closely linked to the burial history of the sediments.

The depth-controlled trends in the chemical composition of the carbonate cement can be explained in terms of changes in pore-water composition which, in turn, depended primarily on the diagenetic transformations in the shales. Trends in the Fe and Mg contents can be related to clay mineral diagenesis, in particular illitization of Fe- and Mg-rich smectites, the rate of which is temperature dependent. The basin-scale zonation is particularly distinct in changes in the iron concentration, showing an increase with increasing burial depth. Coincidentally, the trends in the chemical composition of the pore palaeowater resemble those of the present-day Cambrian formation water.

There is no distinct relationship between the geographic location and carbon isotope values suggesting pervasive migration of organic compounds in the Baltic basin. The variations in carbon isotope composition, however, were influenced by the proximity of sandstone units to shales. Thin sandstone bodies in the shale package are characterised by lighter carbon isotopes in the dolomite cement than those in the thick massive sandstones. Moreover, this influence is observed to increase with increasing burial depth, most probably due to more advanced diagenetic modification of the shales and organic matter in the deeper part of the basin.

In terms of the reservoir quality, some negative influence of the carbonate cement on the porosity of the Cambrian sandstones is observed.

$\delta^{18}\text{O}$ (PDB) values of the ferroan dolomite vary from -5‰ to -14.3‰. The reconstructed temperatures of precipitation range from 27°C in the shallow eastern periphery of the basin to 87°C in western Lithuania. The latter value is close to temperatures reconstructed for the westernmost and deepest part of the basin in northern Poland. A comparison of the burial models with carbonate palaeotemperatures suggests that ferroan dolomite (and ankerite in the west) precipitated during the Silurian and Devonian rapid

burial of the Cambrian succession, and the succeeding latest Palaeozoic uplift.

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