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TEMPERATURE AND ISOTOPIC RELATIONS IN THE MIDDLE MIOCENE SANDSTONES FROM THE UKRAINIAN CARPATHIAN FOREDEEP BASIN – A RECONNAISSANCE STUDY

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Abstract: Studies of the Middle Miocene sandstones in selected wells from the western Ukraine concerned calcite cements, both from isotopic and fluid inclusion aspects. The aim of the reconnaissance study was to find out inclusion – isotopic constraints for the calcite cements in the sandstones. The studied sandstones are subarkosic, sporadically sublithic arenites. The $\delta^{13}C_{VPDB}$ values range from –7.8‰ to –1.3‰, and $\delta^{18}O_{VPDB}$ vary from –8.8 to –4.7‰. Calcite cement was crystallized in the temperature interval from about 32°C to 55°C. Homogenization temperatures of fluid inclusions correspond in general to low values depending on the inclusion character (brine, carbon dioxide). Based on pairs of inclusions trapped together in the cement, the trapping conditions have been estimated for below 60°C and 375 bars that concur with results of isotopic determinations and re-calculations.

Key words: isotopes, fluid inclusions, sandstones, calcite cement, Middle Miocene, Carpathian Foredeep, Ukraine.

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INTRODUCTION

The diagenetic evolution pathways of sandstones are governed by different parameters, including composition of framework grains, pore-water chemistry, tectonic setting of the basin and burial history of the succession (Morad *et al.*, 2000; Mansurbeg *et al.*, 2008). In this context, knowledge of changes in reservoir properties of Middle Miocene strata of the Carpathian Foredeep is important both for the interpretation of their history and for evaluation of the prospects of the oil and gas potential as well as the determination of future hydrocarbon prospection. The object of the present paper are calcite cements of the Middle Miocene sandstones from the western Ukraine. Their detailed petrographic and diagenetic characteristics have been presented by Kuberska *et al.* (2011). The present paper deals with isotopic and fluid inclusion aspects and aims at presentation of the results of the reconnaissance study of the inclusion – isotopic constraints in calcite, an important type of the cement, from the Middle Miocene sandstones in the selected wells from West Ukraine. The goal of this paper is, therefore, to contribute to the further understanding of carbonate cementation in the Middle Miocene sandstones.

GEOLOGICAL BACKGROUND

The geological structure of the Carpathian Foredeep has recently been summarized by Oszczypko *et al.* (2006), Ślączka *et al.* (2006), and Andreyeva-Grigorovich *et al.* (2008). They discussed stratigraphy of the folded Miocene strata at the front of the Ukrainian Carpathians. According to seismic, magnetotelluric and well data, the Carpathian Foredeep is asymmetric and filled in with predominantly clastic sediments of the Miocene age, as much as 6 km thick at the Carpathian front in Ukraine. The molasse strata overlie Permian–Mesozoic terrestrial and shelf sediments and locally occurring Palaeogene deposits. The East European platform basement covered by these Permian–Palaeogene strata and then by the Miocene molasses dips southward beneath the Outer Carpathian units to a distance of at least 50 km (Oszczypko *et al.*, 2006). The Early to Middle Miocene Carpathian Foredeep developed as a peripherical foreland basin related to the advancing Carpathian front. The Palaeozoic–Mesozoic and Cenozoic strata of the Carpathian Foredeep are oil and gas productive (*e.g.*, Popadyuk *et al.*, 2006).

The Miocene deposits in the Ukrainian Carpathian Foredeep occur at depths up to 5,000 m and are represented

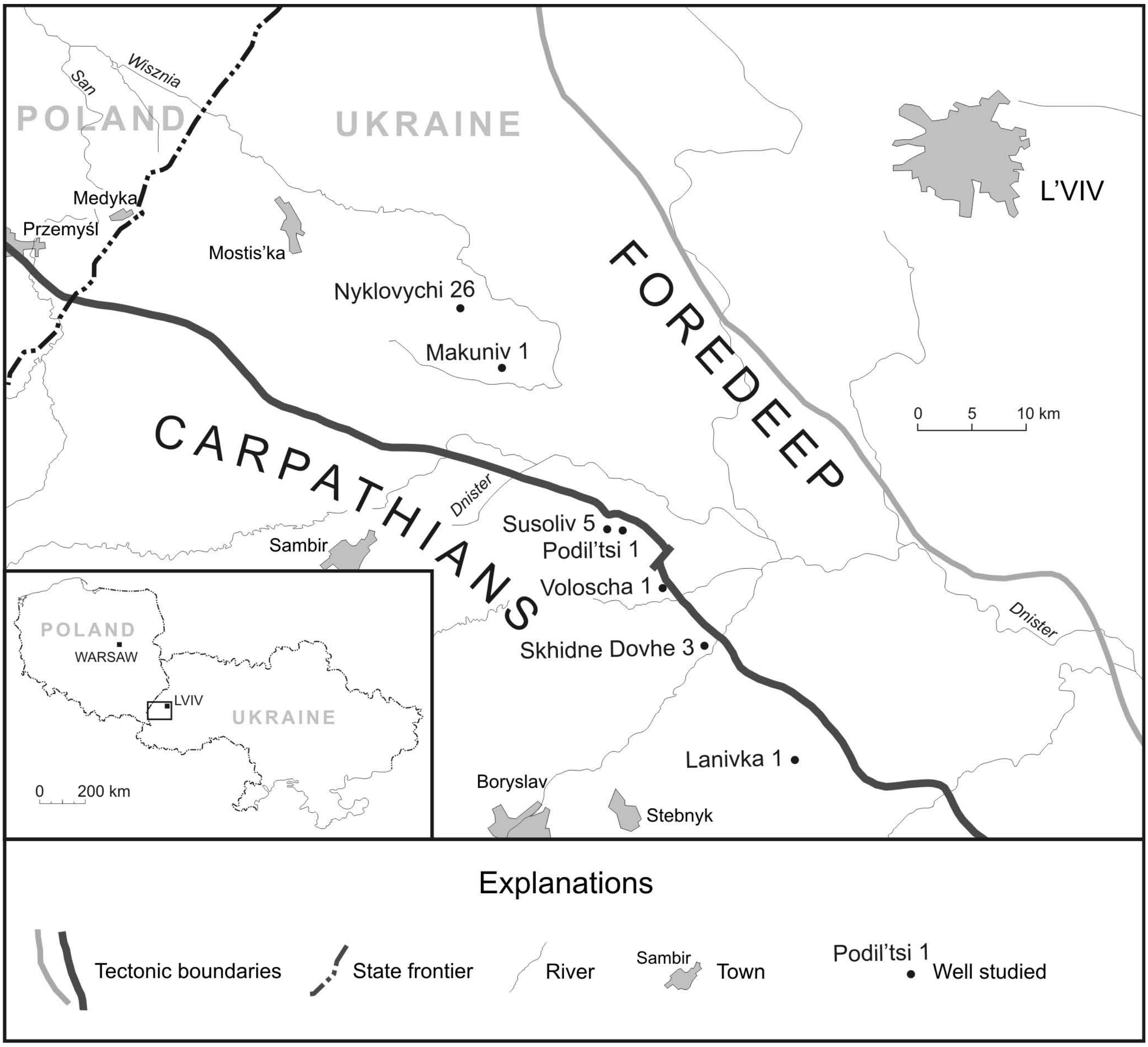

Fig. 1. Schematic locality of wells studied in the present paper

by sandy-clayey rocks, such as: clays, argillite-like clays, aleurolites, quartz and polymictic sandstones, and rare marls, tuffs and tuffites (*e.g.*, Kurovets *et al.*, 2001, 2004). At a depth of 2,000 m the rocks underwent insignificant consolidation with a simultaneous decrease in porosity and permeability and migration of clay minerals by means of halmyrolysis. According to Kurovets *et al.* (2001), the phenomena of quartz regeneration, formation of siliceous cement as well as regenerative halos on the quartz grains are also observed. At this very depth, the Miocene deposits are not consolidated. On the basis of well-drilling data and geophysical investigation in wells, Kurovets and Prytulka (2001) recorded a variation of pH from 7.7 to 9.7 in Miocene strata and a regular increase in this parameter values with depth. They found out that the carbon content in clays ranges from 0.93 and 3.0%, and in sandstones it changes between 0.23 and 1.03%.

We have sampled Middle Miocene sandstones with the aim to analyse their calcite cements. Both petrological analyses were performed and the fluid inclusion observations were conducted, oxygen and carbon isotopic relations determined as well, in calcite cements filling in the intergranular space in the sandstones from wells Susoliv 5, Podil'tsi 1, Voloscha 1, Skhidne Dovhe 3, Nyklovychi 26, Makuniv 1, and Lanivka 1 (West Ukraine, Fig.1).

METHODS

Analytical procedures

Ten sandstone samples were subject to double-sided polishing procedure (according to the standard technique, *e.g.*, Jarmołowicz-Szulc, 2001; modified). Repeated detailed microscopic observations have led to a reduction of the number of samples taking the fluid inclusion aspect into account.

Analytical procedures comprised several stages: sampling and preparation, microscopic evaluation of the material from the point of view of the isotopic and inclusion research, detailed microscopic determinations, analyses and auxiliary studies.

The fluid inclusion observations and measurements were conducted both in the double – sided polished sections (approximate data) and in the polished slabs. SEM analyses were done, too, as it is mentioned by Kuberska *et al.* (2011). The preparations and studies were conducted in the Polish Geological Institute – National Research Institute in Warszawa, while some thin sections were comparatively prepared in Kraków (AGH-UST University of Science and Technology).

Preparation and analytical techniques for fluid inclusion studies

Standard preparation techniques were applied for preparation of sections for fluid inclusion (FI) studies in calcite (Shephard *et al.*, 1985; Jarmołowicz-Szulc, 2001). Double-sided-polished thin sections, 0.1–0.2 mm thick, were obtained due to low-temperature mounting of rocks and successive polishing which uncovered the rock-cement interior. General microscopic observations were conducted applying a polarization microscope both in transmitted and reflected (UV) lights. These comprised a microscopic analysis of fluid inclusions (Leitz Orthoplan), fluorescence studies and microphotography (Nikon microscope and UV device), cold cathodoluminescence studies (CCL 8200 mK3), and microthermometric analyses. The latter included heating and freezing using alternatively a Fluid Inc. System, mounted on a Leitz Orthoplan microscope, and the Lincam equipment with a digital microphotography.

Fluorescence of fluids in inclusions was induced by the ultraviolet reflected light in the plates prepared for the fluid inclusion microthermometry studies. The long–wave light (368 nm) was provided by the 100 W mercury lamp and a set of filters.

The Fluid Inc. System and the Linkam stage were calibrated against melting temperatures of chemicals and phase transitions in synthetic fluid inclusions (SYNFLINC standards, Reynolds, 1993; standards Number 1-3). The uncertainty limits are 0.1°C between –100°C and +100°C and 0.2°C above 100°C. Fluid inclusions in calcite were studied by heating prior to freezing, so that the inclusion volumes were potentially not changed due to ice formation. That first led to the measurement of the homogenization temperatures of inclusions, followed by freezing data (Roedder, 1984; Shephard *et al.*, 1985). Thermometric studies in the heating mode of the primary aqueous inclusions generally lead to estimation of minimum trapping temperatures of fluids in the mineral since it has been assumed that the homogenization temperature represents a minimum temperature of fluid trapping during mineral precipitation (Roedder, 1984).

The estimations of the pressure and temperature conditions of the formation of minerals were based on the crossing isochore technique by use of coexisting carbon dioxide and aqueous inclusions, following the method introduced by Kalyuzhnyj and Koltun (1953). Isochores for carbon dioxide were calculated both with the Flincor program (Brown, 1982) and FLUIDS package Bakker (2003).

Light isotopes – carbon and oxygen

The isotopic studies were conducted by classical methods for calcite cements from selected sandstones. Samples for the analyses were carefully chosen after a detailed petrographic selection. The calcite was extracted from the rocks by "*in situ*" drilling.

Analyses of the isotopic composition of oxygen and carbon in calcite were conducted in the Isotope Laboratory of the Maria Curie-Skłodowska University at Lublin. The method was described by Durakiewicz and Hałas (1994) and Durakiewicz (1996). Gaseous carbon dioxide was released from carbonates during reaction with phosphoric acid. Isotopic measurements of carbon and oxygen were conducted in the modified mass spectrometer MI 1305 with the measurement precision of ± 0.08‰ (one sigma). Measurements were conducted in reference to international standards (Durakiewicz, 1996). Recalculation from $\delta^{18}O_{VPDB}$ to $\delta^{18}O_{VSMOW}$ in calcite was proceeded after the formula of O'Neill (1979): $\delta^{18}O\ (SMOW) = 1.03086\ \delta^{18}\ O\ (PDB) + 30.86$ [‰].

The isotopic data ($\delta^{18}O_{\ PDB}$) for carbonates have been calculated to temperatures according to the following formula after Anderson and Arthur (1983):
$T(°C) = 16.0 - 4.14 \cdot (\delta^{18}OcarbVPDB - \delta^{18}Ow\ VSMOW) + 0.13 \cdot (\delta^{18}OcarbVPDB - \delta^{18}OwVSMOW)^2$,
where $\delta^{18}OcarbVPDB$ – $\delta^{18}O$ in carbonate, $\delta^{18}OwVSMOW$ – $\delta^{18}O$ in water.

RESULTS

Petrological description

The studied sandstones occur as layers of different thickness in the mudstone deposits. The sandstones are fine, unequal, exceptionally medium-grained rocks. They display psammitic, psammitic-aleuritic, or occasionally psammitic-pelitic structure. Arenites and subarkosic wackes, locally sublithic and quartz, have been distinguished according to the nomenclature of Pettijohn *et al.* (1972). Microthermometric studies were conducted on the selected sandstone samples assigned to the subarkosic, sporadically sublithic, arenites.

Quartz is the main component of all varieties of sandstones. It occurs as monocrystalline or, less frequent, polycrystalline grains. Feldspars are the secondary component. Their crystals display either sharp edges, or are occasionally half-rounded. The K-feldspars, which show a blue luminescence in CL, are predominant, while plagioclases are rare. Among lithoclasts, fragments of sedimentary, effusive, magmatic and metamorphic rocks were distinguished. Micas are represented mostly by muscovite, less frequently by biotite. Glauconite is common. Rare bioclasts were noticed in the sandstones.

Matrix, authigenic clay minerals, carbonates, authigenic quartz and sporadic authigenic feldspar were observed in the sandstone cements. Samples that exhibit a high percentage of the carbonate cement were selected for the fluid inclusion and oxygen and carbon isotopic analyses.

Most frequently, the carbonates form the pore-type cement. The basic cement is less frequent. The following types

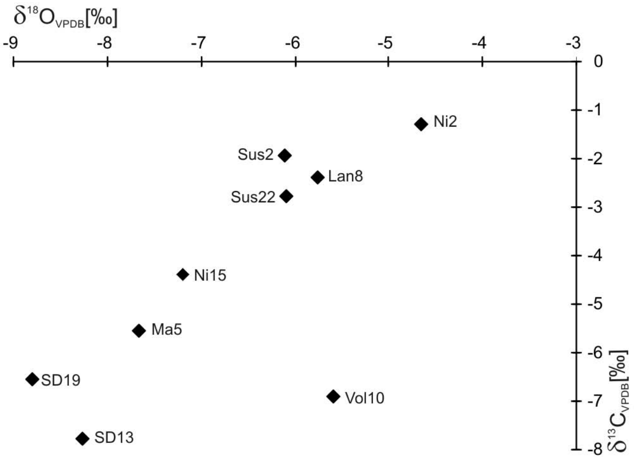

Fig. 2. Distribution of $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ in calcite cement

of the carbonates were distinguished: calcite – mainly Fe-calcite, dolomite and ankerite. The calcite mostly forms anhedral crystals. As it results from the staining analysis of thin sections and SEM studies, the analysed calcite contains an admixture of iron Fe^{2+} and manganese. Dolomite in form of various size rhombohedrons occurs parallel to calcite. Ankerite is less frequent as an individual component of the cement. It is occasionally present in marginal parts of dolomite rhombohedrons.

Stable isotopes

The isotopic results for the calcite samples are shown in Table 1 and in Figure 2. These samples were also an object of the fluid inclusion analysis.

The $\delta^{13}C_{VPDB}$ values in the samples studied change from –7.8‰ (Skhidne Dovhe 3) to –1.3‰ (Nyklovychi 26). For a comparison, the calcite cements from the sandstones in the Tarnogród area in the eastern part of the Polish Carpathian Foredeep generally exhibit $\delta^{13}C$ values in the interval from –4.6 to –0.2 ‰ [PDB] (Maliszewska *et al.*, 2001). In that context, the results for the calcite from the West Ukraine sandstones studied, lie in a wider interval, possibly being controlled by slightly other factors than the Polish ones (*cf.* Marshall, 1992).

The $\delta^{18}O_{VPDB}$ values vary from –8.8‰ (Skhidne Dovhe 3) to –4.7‰ (Nyklovychi 26; Table 1. The adequate $\delta^{18}O_{VSMOW}$ values are from +21.8‰ to +26.1‰.

The C and O isotopic records are not homogeneous and their δ [VPDB] values decrease downward the wells (Fig. 2, Table 1). As it is seen in Figure 2, the points exhibit an almost linear trend of distribution, with the exception of the sample from the Voloscha 1 well. The analytical results of carbon and oxygen isotopes show a significant correlation (r = 0.7). This points to an influence of diagenetic processes onto the isotopic record (see, *e.g.*, Marshall, 1992) and an increase in precipitation temperatures in the studied samples. No decreasing trend with sample depth was noticed.

The $\delta^{18}O$ [VPBD] values may be calculated to temperatures according to the formula of Anderson and Arthur (1983). It is important to introduce a $\delta^{18}O_{VSMOW}$ value for water to the calculations. According to, for instance, Marshall (1992) or Ali (1995), the value of $\delta^{18}O_{water} = -1.2‰$ for the sea water composition should be used. If this value is introduced to the formula, the temperatures of calcite crystallization calculated fall into the interval from 32 to 55°C (Table 1). The minimum and maximum values are shown by the samples from the depth intervals of 1,249.2–1,259.2 m (Nyklovychi 26) and of 1,726.7–1,735 m (Skhidne Dovhe 3), respectively. When adopting the $\delta^{18}O_{VSMOW}$ water equal to –3‰ (the limit of $\delta^{18}O_{VSMOW}$ for ocean water as shown by Sheppard, 1986) to the Anderson and Arthur's formula, the results would change from 55 to 83°C, corresponding to the upper temperature limits.

Fluid inclusion studies

Observations of fluid inclusions in the calcite cement were conducted in the mode of a parallel checking of the double sided – polished section and the adequate thin section.

Table 1

Results of isotopic analyses in calcite for the selected sandstones

Sample number*	Well	Depth (m)	$\delta^{13}C_{VPDB}$ [‰]	$\delta^{18}O_{VPDB}$ [‰]	$\delta^{18}O_{VSMOW}$ [‰]	Temperature (°C)
Ni 15	Nyklovychi 26	1,701.3	-4.39	-7.19	+23.44	45.46
Sus 2	Susoliv 5	2,100.5	-1.95	-6.11	+24.56	39.46
Sus 22	Susoliv 5	2,528.2	-2.78	-6.09	+24.58	39.35
Ni 2	Nyklovychi 26	1,250.5	-1.30	-4.66	+26.06	31.88
SD 13	Skhidne Dovhe 3	1,714.3	-7.76	-8.27	+22.27	51.77
SD 19	Skhidne Dovhe 3	1,726.9	-6.56	-8.80	+21.78	54.97
Ma 5	Makuniv 1	1,847.0	-5.55	-7.66	+22.96	48.17
Vol10	Voloscha 1	2,091.2	-6.91	-5.59	+26.00	36.68
Lan 8	Lanivka 1	1,456.3	-2.40	-5.76	+24.92	37.58

*Samples for isotopic analysis chosen based on petrographic studies. For details see Kuberska *et al.* (2011).

Explanation: Conversion from $\delta^{18}O_{VPDB}$ to $\delta^{18}O_{VSMOW}$ due to the formula of O'Neill (1979). Calculation to temperatures was based on the Anderson and Arthur (1983) formula introducing the $\delta^{18}O_{VSMOW}$ value equal to -1.2 ‰ (after Ali, 1995).

The number of originally selected drilling core samples was finally reduced to some study samples because of the difficulties in the inclusion occurrence, size, complexity and visibility. The conducted studies comprised microscopic observations, microfluorescence, microphotography and heating-freezing steps of fluid inclusions.

Microthermometric measurements of the following phase transitions were made during heating from –100 to +170°C:

1. The temperature of the first melting (T_e= temperature of eutectic), which provides a qualitative estimate of the kinds of dissolved ionic species present;

2. The temperature of melting of the last ice crystal (T_{mice}), which enables the approximate amounts of dissolved chlorides, expressed as NaCl equivalent in wt%, to be determined;

3. The temperature at which clathrates of, for instance, CO_2 and any hydrates of salts disassociate (T_{dcl}), to assess the kinds of dissolved gases and salts that may be present in terms of amount ratios;

4. The temperature of homogenization between the aqueous brine and the vapour phase (T_h), which can be considered as the minimum trapping temperature (Tt) of the inclusion.

Homogenization measurements were also possible in case of one phase inclusions. As it was described by Goldstein and Reynolds (1994) during the freezing of one phase inclusions, the contraction bubble can appear at low temperatures. The subsequent heating of the frozen inclusion results in ice melting and in the disappearance of the bubble (homogenization of fluids within inclusions).

DISCUSSION OF RESULTS

Characteristic of fluid inclusions

Observations of inclusions in the calcite cement were conducted with a comparison between a standard thin section and a two-side polished thin section. In general, inclusions in calcite are quite abundant, their size oscillates from below 1 micrometre to some micrometres.

In some parts, the dimensions of such inclusions preclude microthermometric determinations and create general problems even at the stage of diagnosis, such as determining the amount of phases. In other parts, the inclusions are totally transparent. Occasionally, they are well seen in a standard thin section in contrast to the special two-sided polished and thicker section. In the last case, the cement is often in superposition over the quartz grains.

As it results from the microscopic observations, the oval shapes of the studied inclusions are generally predominant. These inclusions in calcite are mostly one-phase; two-phase inclusion associations *sensu stricto* (liquid and vapour phases) seem to be absent. Even those concerned two-phase inclusions when being observed under the microscope in a moderate magnitude, have appeared to be an artefact. They may either be two co-trapped liquid phases or represent the result of stretching and necking down of the inclusions. Evidently, two-phase inclusions occur in the detrital quartz grains and, therefore, they are ignored in the present paper.

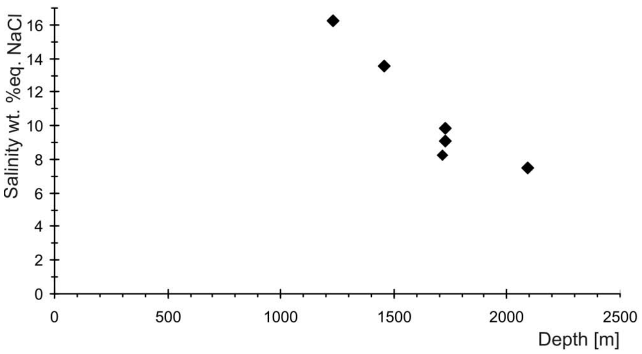

Fig. 3. Trapping conditions for the fluid inclusion pair AQFI and FICO$_2$ (based on Kalyuzhnyi, 1982). Isochores calculated based on Brown (1982). Points correspond to calculated P-T values. Th – homogenization temperature, δ – density of fluid

Beside the oval inclusions in calcite, also rather irregular inclusions are visible in the microscopic image of the samples.

One-phase inclusions in calcite filling in the intergranular space in the sandstones may be described as FI (*fluid inclusions*) of two types, namely: with bright and transparent liquid (L1) and dark liquid (L2). Their sizes change from very small to small dimensions. Their content may be marked as AQFI (*brine inclusions*) and FICO2 (*carbon dioxide inclusions*). Inclusions are mostly individual, their larger associations (“clouds”) are not frequent.

Freezing and heating modes have been applied in the present studies. Some tens of inclusions have shown a standard behaviour when frozen and heated. Many inclusions, however, were difficult to follow during the consecutive heating after freezing due to no result in their phase separation, the dark colour of the image (calcite dark colour) and small size of the inclusions. When frozen by a liquid nitrogen, rare one-phase inclusions in calcite sometimes generated a bubble. The homogenization that followed this bubble formation occurred at +41.1°C for the bright type of inclusions (AQFI) and at +14.6°C for the dark type (FICO2). In this very case, the pair of AQFI and FICO2 inclusions points to low temperatures of trapping of these inclusions in the cement (Fig. 3).

Exemplary results for sample 19 from Skhidne Dovhe 3 well (depth interval of 1,726.7–1,735 m) are shown in Table 2. Freezing proceeded to –70°C, but the characteristic behaviour within the FIAs (fluid inclusion associations) was observed at temperatures above –40°C, as shown there. Characteristic processes as eutectic movement, ice melting, clathrate decomposition and homogenization of different fluids have been registered. In general, the number of inclusions per studied FIAs varied from 8 (Voloscha 1) through 25 (Skhidne Dovhe 3) to 50 (Nyklovychi 26) ones. Altogether, about 160 inclusions in FIAs and as individuals were studied in the calcite cement.

The results of microthermometric FI studies are presented in Table 3 together with salinities of fluids expressed in wt.% eq. NaCl, based on calculations by Flincor program (Brown, 1982). The relationship between present occurrence of the sandstones and salinity of fluids in inclusions in the calcite cement is shown in Fig. 4.

Table 2

The example of phase changes at increasing temperatures after freezing to –70°C for inclusion associations in calcite from Skhidne Dovhe 3/19 (depth interval 1,726.7–1,735 m)

Process	Skhidne Dovhe 3 / 19			
Homogenization			Th2 = +14.6	Th1 = +41.1
Clathrate melting	T dcl = +3.8			
Ice melting	Tm = -5.9	Tm = - 3.5	Tm = -3.3	Tm = - 6.5
Eutectic temperature	Te = -35			Te = -32.7

Explanation: Skhidne Dovhe 3 / 19 - Skhidne Dovhe 3 well, sample 19; AQFI - brine inclusions; FICO2 - CO2-bearing inclusions; Te - eutectic temperature; Tm - ice melting temperature; T dcl - clathrate melting; Th1, Th2 - homogenization temperatures for different types of inclusion fluids, AQFI and FICO2, respectively.

Temperature measurements

Fluid inclusions observed in the calcite cement in the sandstones in the wells studied are mostly one-phase. They are of two types – transparent (L1) and dark (L2) (*e.g.*, Skhidne Dovhe 3, Lanivka 1). Their size ranges from below 1 µm to the interval of 1–2 µm. Some of them remain unchanged: they show no characteristic features in the heating-freezing mode. Already, the one-phase character of the inclusions points to low temperatures of formation of the cement – at about 50°C (Shephard *et al.*, 1985; Burruss *et al.*, 1987). Sometimes a bubble does not appear in the inclusions when cooled. In such cases, however, the first melting may be observed at temperatures below –26°C (*e.g.*, Lanivka 1), in most cases at about –34°C. This indicates the solution of the NaCl-$CaCl_2$-$MgCl_2$-H_2O system (Shephard *et al.*, 1985). The ice melting temperature of –9.6°C shows that the fluid exhibited a salinity of about 13.52 wt.% eq. NaCl (Brown, 1982; Bodnar, 1990).

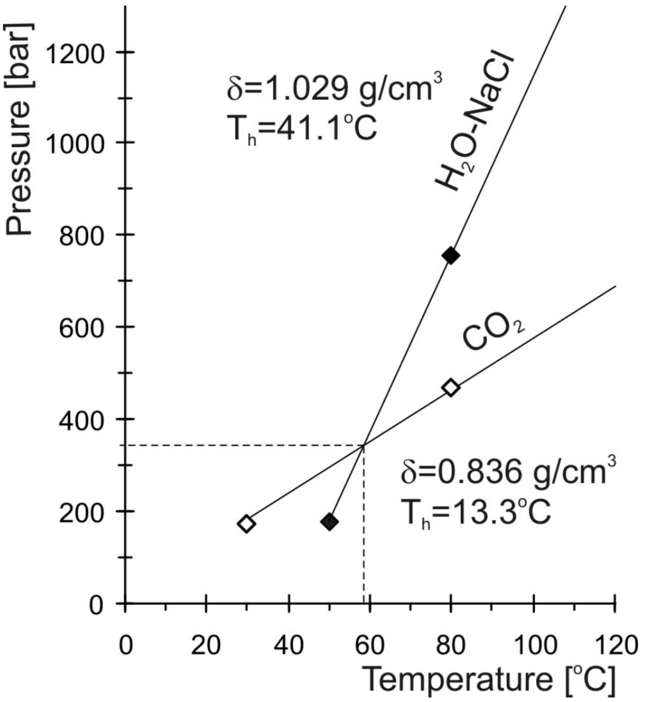

Fig. 4. Relationship between depth of present occurrence of sandstones and salinity of inclusions in calcite cement

Freezing and heating procedure was applied to the calcite cements from the rocks from different depths. In general, the homogenization temperatures fall into the interval from 41.1 to 146°C, this last value, however being obtained for the two-phase inclusion displaying evident features of stretching and accompanied by one-phase inclusion.

The eutectic temperatures (first melting observed), generally below –21°C determined on 85 inclusions point, to the presence of calcium and/or magnesium ions in the fluid together with NaCl (Shepherd *et al.*, 1985). The ice melting temperatures between –6.5 and –5.9°C suggest a low salinity of the fluid changing from 9.05 to 9.84 wt.% eq. NaCl,

Table 3

Microthermometric results for fluid inclusions in the calcite cements of sandstones in selected wells

Well/Sample	Depth (m)	T h (°C)	Te (°C)	T m (°C)	Salinity wt% eq. NaCl
Skhidne Dovhe 3 sample 13	(1,711–1,720) 1,714.3	146	ca –35	-5.3	8.23
Skhidne Dovhe 3 sample 19	(1,726.7–1,735) 1,726.9	+13.3 +14.1 +41.1	–32.7	-6.5 to -5.9	9.05 9.84
Lanivka 1	(1,455–1,465) 1,456.3		about –34	-9.6	13.52
Susoliv 5 sample 22	(2,520.4–2,535) 2,528.2		about –30	-6.5 -6.0	9.84 9.84
Podil'tsi 1	(1,231.7–1,243.2) 1,231.8	+8.5	about –40	-12.3	16.24
Voloscha 1sample 10	(2,090–2,100) 2,091.2		–33.4	-4.8	7.53

Explanation: Skhidne Dovhe 3 s. 19 - Skhidne Dovhe 3 well, sample 19; Te - eutectic temperature; Tm - ice melting temperature; T h - homogenization temperatures. Depth intervals in parantheses.

i.e. between about 9 and 10 wt.% eq. NaCl. (Fig. 4). The fluid densities in the inclusions in calcite from Skhidne Dovhe 3 are about 1.06 g/cm^3, while in Lanivka 1 – 1.09 g/cm^3.

IMPLICATIONS AND CONCLUSIONS

Studies on chemical diagenesis of various sandstones, including those of Miocene age, have been conducted by different authors from the isotopic and mineralogical points of view (*e.g.*, Ali, 1995; Chowdhury & Noble, 1996; Sanyal *et al.*, 2005). In general, the δ^{18}O value of calcium carbonate cement depends on the temperature of its crystallization and on the δ^{18}O value of the ambient water. Calcium carbonate precipitating at shallow level should reflect the δ^{18}O value of local groundwater, however, its subsequent value can alter this inherited value. The δ^{18}O value of carbonate cement associated with the sandstone, therefore, bears the imprint of burial. Analyses of carbonates, cherts, phosphates and glauconites from marine sediments of different ages have revealed mineral – $\delta^{18}O_{VSMOW}$ [‰] trends with time (Sheppard, 1986). The isotopic composition of the ancient ocean water is reported there to be about 0 and –3‰ for δ^{18}O (at least since 2,500 Ma; Sheppard, 1986). If the $\delta^{18}O_{VSMOW}$ equal to –3‰ were adopted to recalculation of the oxygen isotopic results, the temperatures would be in the range of 55°C and 83°C in the present paper. This would indicate such an interval of crystallization temperatures of the calcite cement. On the other hand, according to Lear *et al.* (2000), based on studies of benthic foraminiferal calcite, the value of δ^{18}O water in the Badenian and Sarmatian was about 0.5‰ lower than at present. Most of researchers are of opinion to use the δ^{18}Owater = –1.2 [‰] for the seawater composition prior to the establishment of polar ice caps (*e.g.*, Marshall, 1992; Ali, 1995). Therefore, this value should be used and has been introduced in the present paper to the Anderson and Arthur's (1983) formula. The palaeotemperatures of the calcite cement in the studied sandstones are between 32°C and 55°C, as it is shown in Table 1.

Ali (1995) presents cement stratigraphy and diagenesis of the Miocene mixed carbonates in Malaysia. For calcite, he obtains δ^{18}O isotopic values that show a decrease from –2.1 ‰ to –5.3‰ [PDB]. The decrease in values indicates an increase in precipitation temperatures with burial. Mansurbeg *et al.* (2008) show δ^{18}O values of the eugenic concretionary calcite in the sandstones in the Shetland-Faroes Basin in the interval from –7.7 ‰ to –1 ‰ [PDB]. They believe precipitation temperatures to be of (15–50) °C if precipitation is assumed to have occurred from marine pore waters with unmodified oxygen isotopic composition (–1.2 [‰] relative to SMOW). The corresponding $\delta^{13}C_{VPDB}$ values are there from –17.8‰ to +5.3‰, and according to these authors they indicate derivation of carbon from the bacterial sulphate reduction and from microbial methanogenesis, respectively.

The δ^{13}C results for the calcite cement from the Miocene sandstones in Ukraine are higher in values. They are in the interval from –7.76‰ to –1.3‰ [VPDB]. They overlap the interval between –4‰ and –11‰, characteristic for the carbonates of biogenic origin as discussed by Chowdhury and Noble (1996), and the interval from –8.5 to –1.7 (Mansurbeg *et al.*, 2008) that indicates a low to moderate input of ^{12}C from the oxidation of the organic matter.

The studied samples from the wells in the western Ukraine derive from various depths across 1,700 m (see Table 2). Isotopes and inclusions were analysed in calcite, that is a mineral more susceptible to the influence of the external factors, such as pressure and temperature than, for instance, quartz.

There are two main problems in the studies of diagenesis of the rocks and the interpretation of the results of fluid inclusion studies. Even when the proofs point to the inclusion trapping during crystallization, the melting and homogenization temperatures may have variable values due to re- equilibration of inclusions (Goldstein & Reynolds, 1994). The deep burial represents the second problem, since it can cause inclusion stretching and leakage, so that the inclusions are not a closed system during heating due to burial (Burruss, 1987; Goldstein & Reynolds, 1994). However, this does not seem to be the case of the sandstones under research.

Only in one sample (Skhidne Dovhe 3, sample 13, depth interval of 1,726.7–1,735 m) the measured exceptional value of 164°C may be concerned either as such a case, or it may reflect the homogenization of two liquid inclusions that together create an apparent two-phase one. Despite this one extreme value, other microthermometric results are low and place themselves either around 50°C or below 20°C. They depend on the type of the fluid filling in the inclusion vacuole, *i.e.* brine (AQFI) and carbon dioxide (FICO2). In one case (Skhidne Dovhe 3, sample 19, depth interval of 1,726.7–1,735 m), it was possible to find out the common trapping conditions of the AQFI and FICO2 pair (Fig. 4).

As it is shown in Figure 4, the trapping conditions of the brine and carbon dioxide fluids in calcite are estimated for below 60°C and 375 bars.

If both isotopic and fluid inclusion data discussed above are taken into account, they may point out to the $\delta^{18}O_{VSMOW}$ composition of the fluid responsible for calcite cement formation, higher than –3‰, of moderate salinity and density. Salinity of the fluid shows a decreasing tendency with depth (Fig. 4). Fluid inclusion and isotope results give temperature and pressure constrains to the calcite cements studied.

In conclusion, in the sandstones from the selected wells in the western Ukraine (Susoliv 5, Podil'tsi 1, Voloscha 1, Skhidne Dovhe 3, Nyklovychi 26, Makuniv 1, Lanivka 1), the calcite cements were formed generally in similar conditions: low temperatures of below 60°C and at pressures of about 375 bars (*e.g.*, Skhidne Dovhe 3). The fluid was the CO_2-bearing one, of moderate salinity (of about 10% and about 13–16 wt% eq. NaCl), moderate isotopic composition and density of about 1.1 g/cm^3.

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