

Isotopic composition of dolomite associated with Middle Miocene Badenian anhydrites in the Carpathian Foredeep Basin of SE Poland

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Dolomite is a quite common, although usually minor, constituent of the Badenian sulphate deposits of the Carpathian Foredeep Basin. In the autochthonous member of the Wola Różaniecka 7 borehole (SE Poland) which contains well preserved, large anhydritic pseudomorphs after selenitic gypsum, dolomite constitutes up to 75% of the rock volume, the rest being anhydrite. Dolomites mostly show peloidal clotted microfabrics typical of microbialites and are interpreted as products of microbially induced precipitation and/or dolomitisation at temperatures around 40°C (as interpreted from the $\delta^{18}\text{O}$ values that range from 0.4 to 2.6‰ VPDB) and in water not very distant from equilibrium with atmospheric carbon dioxide ($\delta^{13}\text{C}$ values usually within the range of +1.0 to +1.6‰ VPDB). Dolomites associated with laminated anhydrite show similar $\delta^{18}\text{O}$ values (from +0.9 to +1.5‰ VPDB) and different $\delta^{13}\text{C}$ values (from –9.2 to –12.6‰ VPDB) than the dolomites from the peloidal clotted microfabrics, and are linked to dolomitisation of carbonate mud by evaporitic hypersaline fluids in the early diagenetic/shallow burial environment. The deposits of the laminated anhydrite originated mostly in a deeper, probably stratified, basin, and carbon from the oxidation of organic matter dominated the pool of carbonate ions. $^{87}\text{Sr}/^{86}\text{Sr}$ values of anhydrite (0.71058–0.71947) and carbonates (0.71024–0.71148) in both members of the Wola Różaniecka 7 borehole are much higher than the values of contemporaneous Badenian seawater. They indicate strong modification of seawater-derived brines by highly radiogenic continental waters.

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INTRODUCTION

Interpretations of the sedimentary and diagenetic environments of ancient anhydrites are based on modern facies analogues and original features of the calcium sulphate minerals. Some Neogene sequences contain both primary gypsum and anhydrite deposits with common pseudomorphic features, inherited from the precursor gypsum deposits, giving thus an opportunity to compare both mineral facies and to interpret the original sedimentary facies of the anhydrite. One of these examples may be found in the Middle Miocene Badenian evaporite basin of the Carpathian Foredeep, which was a depression with the brine level located below the contemporaneous sea level (Peryt, 2001, 2006; Babel, 2004, 2007). These evaporites consist of calcium sulphate and rarely of halite. The presence of potash is still under debate (Hryniv *et al.*, 2007, with references therein). In addition, limestones with gypsum pseudomorphs occur locally in the evaporite section; they were

interpreted by Gąsiewicz (2010, with references therein) as formed in a sedimentary, transitional milieu between the carbonate and the gypsum domains.

In the Polish Carpathian Foredeep primary gypsum occurs only along the margin of the basin and secondary anhydrite deposits are widely distributed in a more central basin location (Fig. 1; Kasprzyk, 2003, with references therein). This study focuses on the anhydrite section (Wola Różaniecka 7) located in SE Poland (Fig. 1) that contains important volumes of dolomite in various parts of the section (Figs. 2 and 3), with calcite being a subordinate component. The occurrence of dolomite was earlier recorded in the Badenian gypsum and anhydrite, mostly in the form of peloidal dolomitic matrix in nodular anhydrite, dolomite laminae in regularly laminated anhydrite, and clasts of dolomite in anhydrite breccias (e.g., Kubica, 1992; Peryt and Kasprzyk, 1992a, b, fig. 4; Kasprzyk 1993, 1995a, 2003, table 2; Kasprzyk and Ortí, 1998), but its origin did not attract attention. Its detailed study, however, can contribute substantially to the understanding of the system from which the

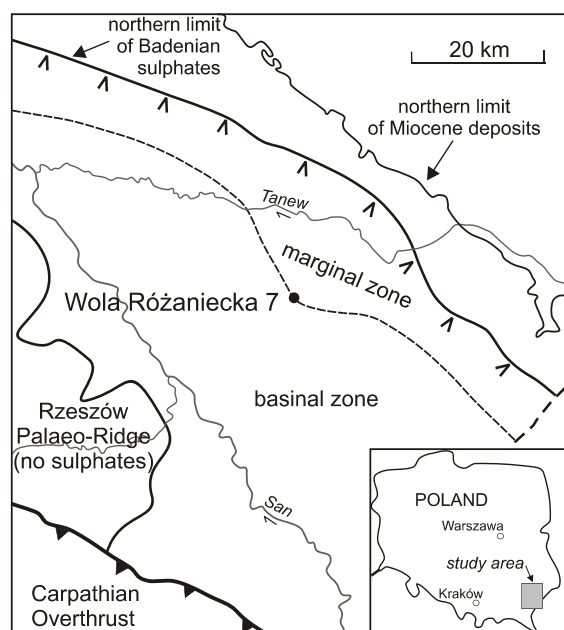


Fig. 1. Location map of the Wola Ró aniicka 7 borehole

evaporites precipitated. The aim of this paper is to characterize the dolomites and the hosting sulphate facies, based on carbon and oxygen isotopes of carbonates combined with the study of strontium isotopes of the carbonates and sulphates, and sulphur and oxygen isotopes of the sulphates.

GEOLOGICAL FRAMEWORK

The Polish Carpathian Foredeep Basin (PCFB) developed during the Early and Mid Miocene as a peripheral flexural foreland basin in front of the advancing Carpathian front (Oszczypko, 2006; Oszczypko *et al.*, 2006). Lower Miocene strata are mainly terrestrial in origin, and Middle Miocene deposits (from a few hundred metres in the northern part of the PCFB to 3500 m in its southeastern part) were developed in marine settings (Oszczypko, 2006). A minor constituent of the stratigraphic column are evaporites belonging to the Badenian Krzy anowice and Wieliczka formations (Alexandrowicz *et al.*, 1982). The calcareous nannoplankton indicates that the evaporites were deposited during the Serravallian (NN6 zone – Peryt, 1997, 1999; Andreyeva-Grigorovich *et al.*, 2003), with the onset of evaporite sedimentation shortly after 13.81 Ma (de Leeuw *et al.*, 2010). In the northern and northeastern part of the foredeep, a sulphate platform (20 km wide) was developed that is composed of sulphates (several tens of metres thick) formed mainly in salina environments (Kasprzyk, 1993; Peryt *et al.*, 1994; B bel, 2004). These salina environments were subject to the inflow of waters from the land, particularly during the deposition of the upper part of the gypsum sequence (e.g., Kasprzyk, 1993; Peryt, 1996; B bel, 1999).

Two gypsum members, building the marginal part of the sulphate platform, are distinguished in the Badenian of the

northern part of Carpathian Foredeep: a lower member of mostly autochthonous, selenitic facies, and an upper member composed mainly of allochthonous, clastic deposits (Kasprzyk, 1999). Towards the south, in the subsurface, gypsum is replaced by anhydrite. Kasprzyk and Ortí (1998) recognized two anhydrite members within the Badenian evaporite deposits. The lower anhydrite member, with well preserved, large pseudomorphs after selenitic gypsum, formed by syndepositional anhydritization in the sulphate platform setting, and the upper member anhydrite that originated due to both syndepositional, interstitial anhydrite growth and to early to late diagenetic replacement of gypsum in the basin centre and on the platform (Kasprzyk and Ortí, 1998; Kasprzyk, 2003). Anhydritization patterns observed in the Badenian evaporite basin (Kasprzyk, 1995b, 2003). The overlying laminated anhydrite and breccias, widely distributed in the foredeep, are equivalent to the upper (clastic, allochthonous) gypsum member (Kasprzyk and Ortí, 1998). In the southern part of the foredeep the anhydrite deposits, up to 20 m-thick, consist of laminated anhydrite with breccia intercalations (Kasprzyk and Ortí, 1998; Peryt *et al.*, 1998; Peryt, 2000; Kasprzyk, 2003), and change laterally into halite deposits (Garlicki, 1979).

The Wola Ró aniicka 7 borehole section is composed of two parts. The lower, autochthonous member contains nodular anhydrite (1.7 m), with common elongated nodules resembling pseudomorphs after large gypsum crystals (Fig. 2) which are embedded in a carbonate-clay matrix (very abundant in places), followed by bedded anhydrite and then by a 9 m thick unit of pseudomorphic anhydrite after large selenite gypsum crystals (Figs. 2 and 3) with common carbonate streaks, laminated intervals, and cement between the sulphate crystals (Fig. 3). The uppermost part of the pseudomorphic anhydrite after large gypsum crystals appears slightly brecciated, and it is followed by the upper, clastic member (Fig. 2) of a total thickness of around 25 m. Anhydrite breccia deposits (9.0 m thick) occurs in the lower part of the clastic member and are followed by laminated, often distorted, anhydrite (Figs. 2 and 4) with breccia intercalations (Peryt, 2000, fig. 7) and carbonate laminae (Fig. 4A); the total thickness of these mostly laminated deposits is 14 m. Laminated anhydrite shows minor disturbances (folding) of lamina sets and truncations of laminae by erosional surfaces and often contains clastic anhydrite laminae showing grading (Peryt, 2000, fig. 4); lamination is very regular, planar (Fig. 4B) or slightly lenticular. The top of the anhydrite sequence consists of recrystallized gypsum of brecciated appearance (2 m thick). Overall, the lithological succession of the Wola Ró aniicka 7 borehole is characteristic of a sulphate platform/sulphate basin transition (Peryt, 2000; Fig. 1).

The Badenian anhydrites of the Wola Ró aniicka area are overlaid by *ca.* 1 km of Miocene siliciclastic deposits. As the erosion of Miocene strata in the area investigated was roughly 500–780 m (Dudek, 1999), the maximum burial of anhydrite can be estimated as more than 1.5 km.

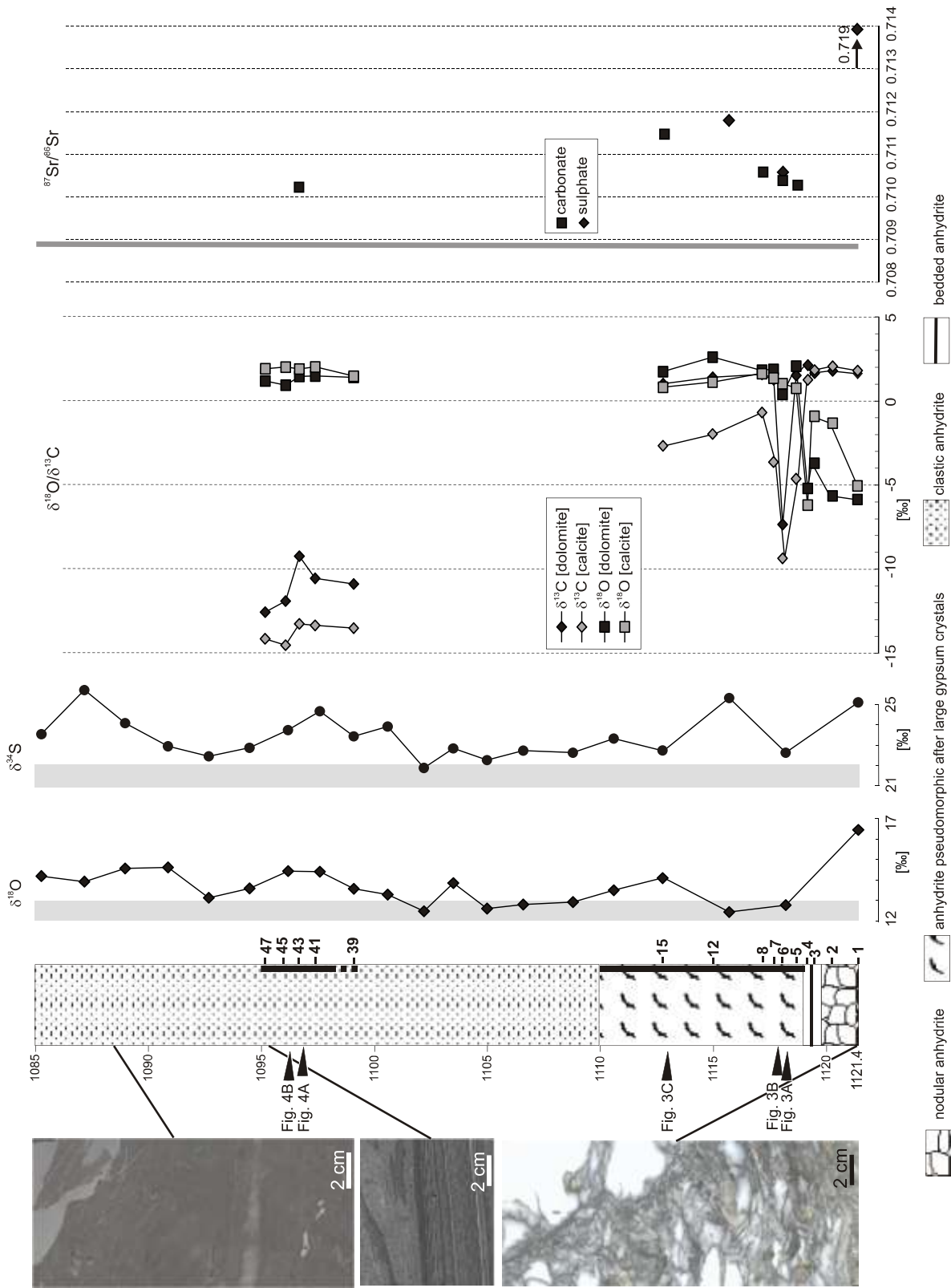


Fig. 2. Lithology and geochemistry of the Wola Ró aniecka 7 anhydrite section showing the location of the samples (right side of lithological column) subjected to geochemical study

Black bar within the lithological column indicates those intervals with an important content of carbonates (up to 75% in the lower part of the section and up to 10% in its upper part). Sulphur and oxygen isotopic composition of anhydrite after Peryt *et al.* (2002); contemporaneous seawater $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values (grey fields) after Paytan *et al.* (1998) and Zak *et al.* (1980); contemporaneous $^{87}\text{Sr}/^{86}\text{Sr}$ ocean water ratio after McArthur *et al.* (2001)

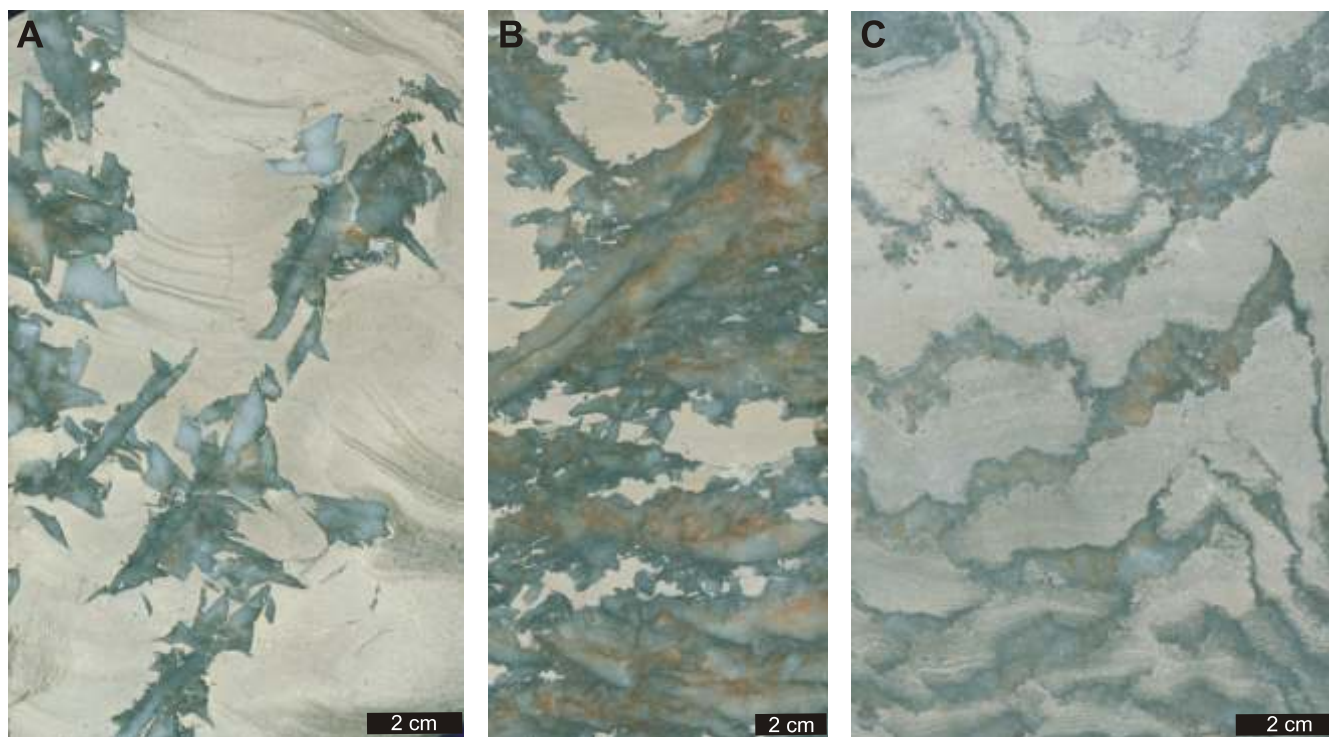


Fig. 3A – laminated dolomite microbialites (beige) with rare pseudomorphs after selenite gypsum crystals, sample 6; **B** – dolomitic sediment (beige) filling intercrystalline porosity between former selenitic gypsum crystals (now anhydrite pseudomorphs), sample 7; **C** – dolomitic stromatolites (beige) with intercalations of selenite (?originally grass-like) gypsum (now anhydrite pseudomorphs), sample 15

MATERIAL AND METHODS

The research was based on petrological observations of 20 thin sections that were stained with Alizarin Red S and potassium ferricyanide (as described by Dickson, 1966) to assist the identification of dolomite and to assess the Fe content of the carbonates. In addition, three selected samples (nos. 6, 15 and 39) were subject to XRD examination which showed that dolomite is the main (sample 6) or the only carbonate mineral present (samples 15 and 39). Four thin sections were studied with cathodoluminescence (CL). In addition, Scanning Electron Microscopy (SEM) examination (mostly in backscattered mode) and microprobe analyses were carried out. Sixteen carbonate samples were selected for oxygen and carbon isotope determination in the Mass Spectrometry Laboratory at the Maria Curie-Skłodowska University in Lublin, Poland; mixtures of dolomite and calcite were analysed. For the isotopic analyses, CO₂ gas was extracted from the samples by reaction of dolomite with H₃PO₄ (McCrea, 1950) at 50°C in a vacuum line for at least 24 h. Results for $\delta^{18}\text{O}$ were corrected for the acid fractionation according to Rosenbaum and Sheppard (1986). The gas was purified of H₂O on a P₂O₅ trap and collected on a cold finger. Isotopic compositions were analysed using a modified Russian *MII305* triple – collector mass spectrometer equipped with a gas ion source. Isobaric correction was applied. After subsequent normalization to measured international standards, the isotopic composition was expressed in per mille (‰) relative to the VPDB international standard and sep-

arately to PDB. Analytical precision of both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in samples and standards was better than $\pm 0.08\text{‰}$.

⁸⁷Sr/⁸⁶Sr ratios were determined in five carbonate samples and three anhydrite samples at the Isotope Geochemistry Laboratory, Kraków Research Centre of Institute of Geological Sciences, Polish Academy of Sciences, following the procedure described by Peryt *et al.* (2010). Dissolved samples were first loaded on a standard cation column (*DOWEX 50W-X12* resin). The collected Sr fraction was further purified on an Eichrom Sr-spec resin and, after converting to nitrates, the sample was analysed on an *MC ICPMS Neptune* in 2% HNO₃. Isotopic ratios were corrected for instrumental mass bias by normalizing to ⁸⁶Sr/⁸⁸Sr = 0.1194 using exponential law. Reproducibility of the SRM987 over the period of analyses was ⁸⁷Sr/⁸⁶Sr = 0.710263 ± 13 (2SE, n = 4), which is identical with long term reproducibility for nearly 2 years ⁸⁷Sr/⁸⁶Sr = 0.710263 ± 13 (2SE, n = 180). The results obtained were normalized to the recommended SRM987 value ⁸⁷Sr/⁸⁶Sr = 0.710248. Precision of individual of ⁸⁷Sr/⁸⁶Sr ratios in [Table 1](#) refers to the last significant digits and is at 2SE level.

RESULTS

PETROLOGY

Carbonates occurring in the autochthonous member of the Wola Ró aniecka 7 anhydrite section are dolomite and, sec-

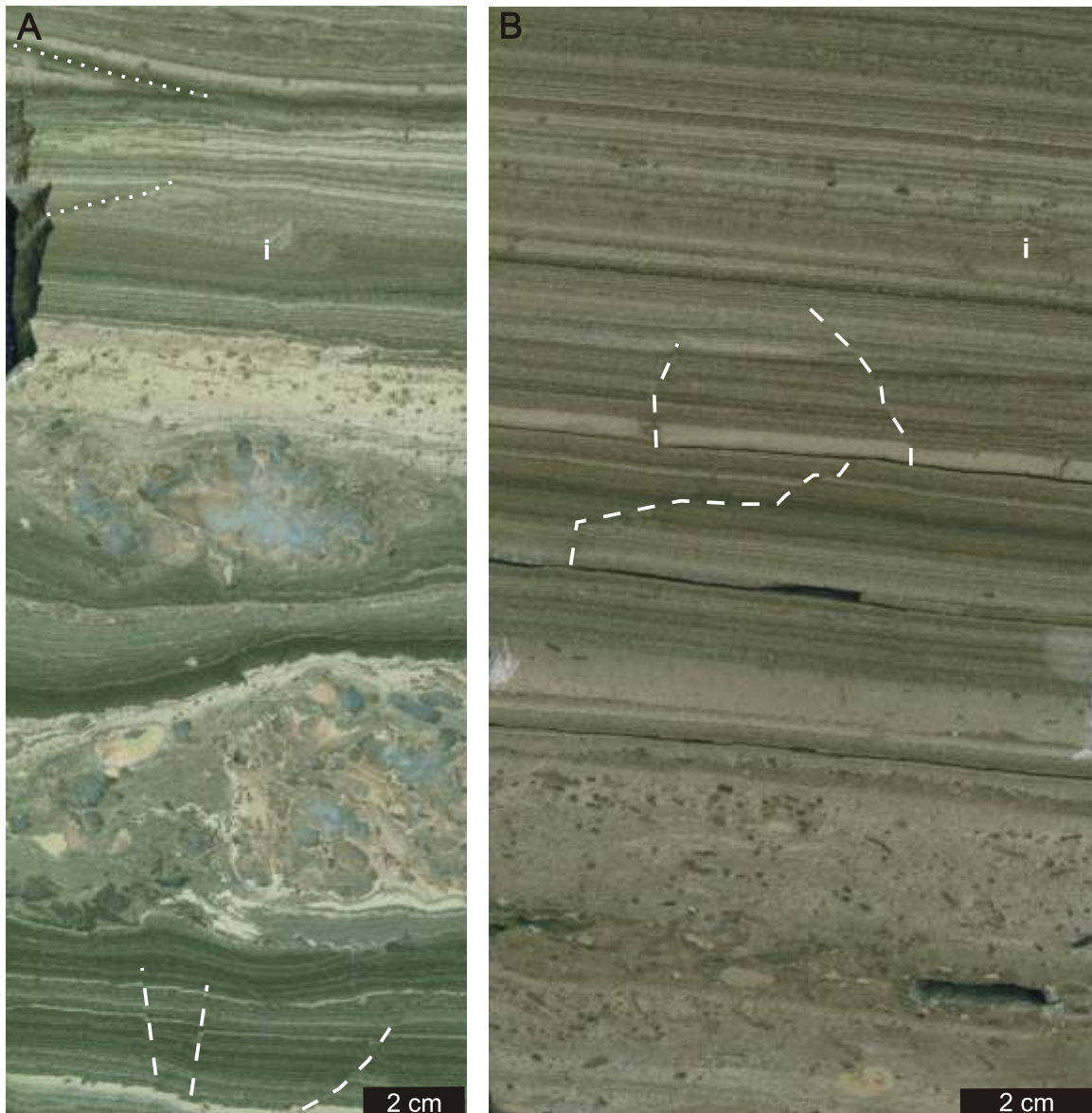


Fig. 4A – laminated anhydrite showing common disturbances (i) that are partly due to nodule growths and minute faults (broken white lines), sample 43; **B** – clastic anhydrite, with rounded anhydrite clasts (<1 cm across), covered by planar laminated anhydrite showing grading in its lower part and small faults (broken lines) and minor disturbances (i), sample 45

ondarily in some samples only, calcite; they fill the spaces between the anhydrite crystals (pseudomorphs after the former gypsum selenite crystals) and/or they are a constituent of anhydrite-carbonate microbial laminites (Figs. 3 and 5A–C). In both cases, they exhibit peloidal or dense micritic fabrics with distinct lamination (Fig. 5A–C) of possible microbial origin. The peloids probably comprise mainly microbial precipitates and locally fecal pellets (Fig. 6). The carbonates contain neither microfauna nor bioclasts. Very little terrigenous material (individual quartz or feldspar grains or mica flakes) was observed.

Dolomicrite is the dominant constituent of the peloids (Fig. 7A, B, E, F) whereas calcite forms cement that occludes pore spaces between the peloids (Fig. 7A–C). Dolomite crystals are a few μm across and calcite crystals are up to 10 μm in

size. Other important authigenic mineral is celestite that usually constitutes up to few percent of the carbonates (Fig. 7B–F). It forms variably-sized (up to several tens of μm) crystals homogeneously dispersed within the rock. Additionally, variable amounts of anhydrite cement are present (Figs. 6 and 7).

The carbonates of the allochthonous member of the Wola Ró aniecka 7 borehole form submillimetric to 1 cm-thick laminae made of dolomicrite (up to 2 μm in size) with significant volumes of intercrystalline porosity (Fig. 8F); these dolomitic laminae are sandwiched between anhydrite laminae (Figs. 4 and 5D) deposited in a deep basin from suspension; some gypsum grains crystallized in the upper part of the brine body and others were derived from erosion and redeposition of older gypsum sediments (Peryt, 2000). The laminae con-

Table 1

Isotope data of the Badenian evaporites of the Wola Ró aniecka 7 borehole
(italics indicate strontium isotope results of anhydrite samples)

Sample number	Depth [m]	$\delta^{13}\text{C}_{\text{VPB}}$ [‰]	$\delta^{18}\text{O}_{\text{VPB}}$ [‰]	$\delta^{13}\text{C}_{\text{VPB}}$ [‰]	$\delta^{18}\text{O}_{\text{VPDB}}$ [‰]	$^{87}\text{Sr}/^{86}\text{Sr}$	2SE (measurement precision)
		calcite		dolomite			
1	1121.4	1.8	-5.05	1.62	-5.86	<i>0.719468</i>	0.000014
2	1120.3	2.06	-1.32	1.78	-5.65		
3	1119.5	1.83	-0.91	1.65	-3.7		
4	1119.2	1.25	-6.2	2.12	-5.2		
5	1118.8	-4.63	0.75	1.51	2.07	0.710276	0.000008
6	1118.2	-9.37	1.02	-7.35	0.38	<i>0.710585</i>	0.000009
						<i>0.710391</i>	0.000007
7	1117.8	-3.64	1.36	1.26	1.87		
8	1117.2	-0.69	1.61	1.56	1.83	0.710586	0.000007
11	1115.7					<i>0.711800</i>	0.000008
12	1115.1	-1.98	1.11	1.4	2.6		
15	1112.9	-2.68	0.8	1.01	1.73	0.711476	0.000009
39	1099.2	-13.5	1.48	-10.88	1.41		
41	1097.5	-13.33	2.03	-10.54	1.5		

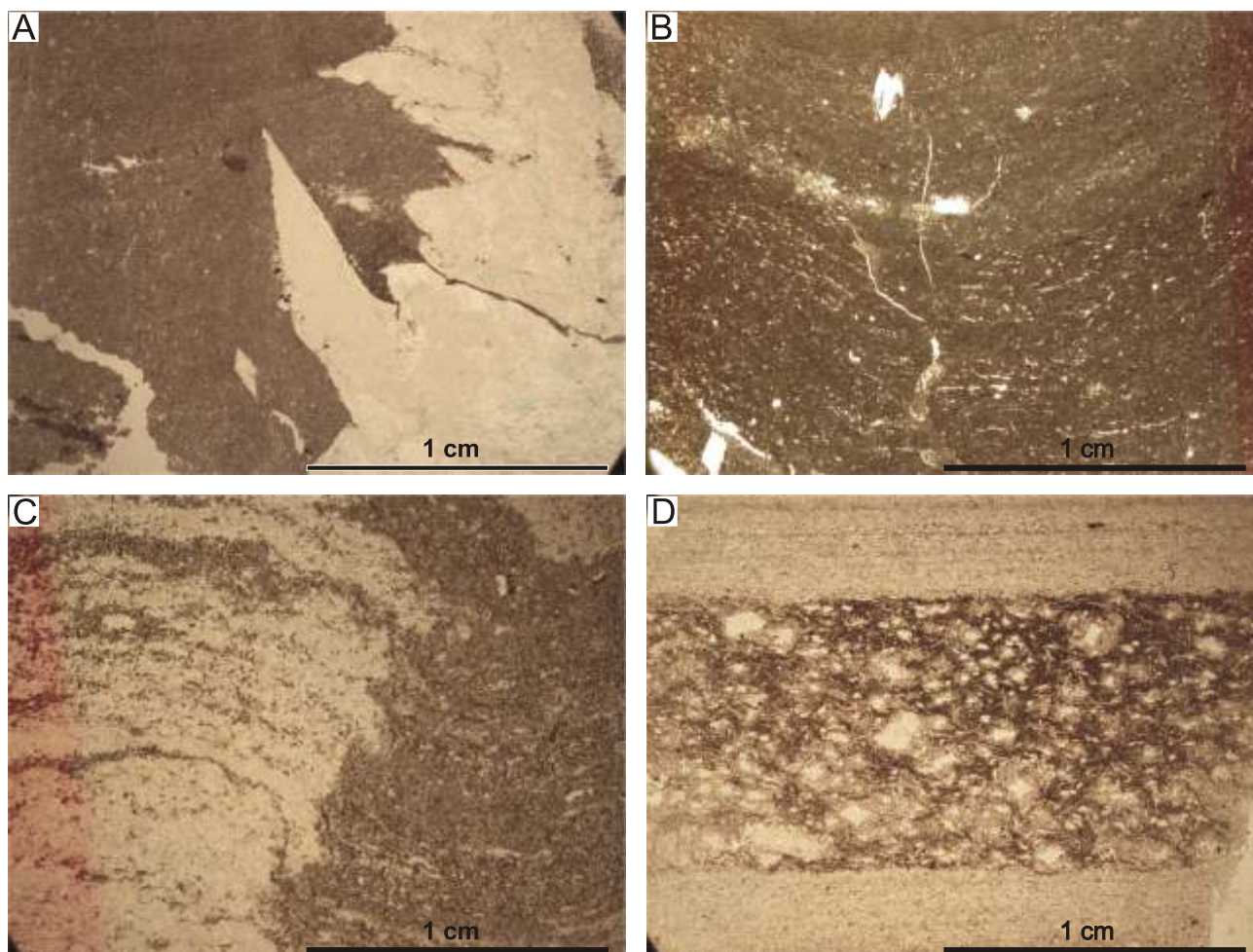


Fig. 5. Transmitted light photomicrographs of thin sections, parallel polars

A – laminated massive carbonate mud (left) filling spaces between the former gypsum crystals – now converted to anhydrite (right), sample 5; **B** – laminated peloidal filling of the intercrystalline pore space; white is anhydrite pseudomorphed after lenticular gypsum crystals that occludes inter-peloidal and fracture pores, sample 6; **C** – carbonate-gypsum stromatolite; small stromatolitic dome (left) was composed mainly of gypsum (now converted to anhydrite) with only few carbonate laminae while interstitial space (right) is filled with laminated carbonate mud, sample 8; **D** – thick carbonate lamina in fine laminated anhydrite; carbonate mud is crowded with numerous anhydrite laths and nodules, sample 39

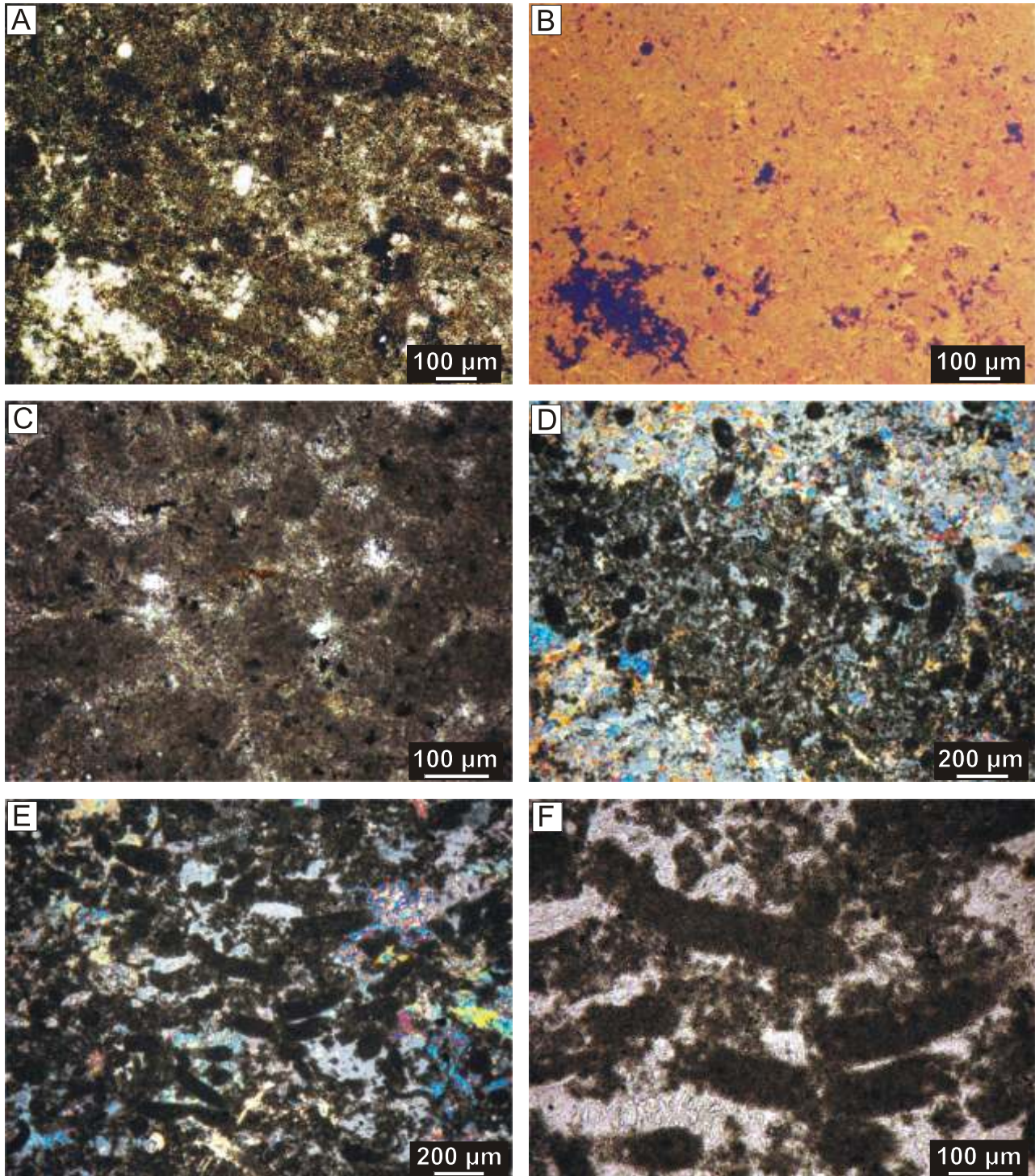


Fig. 6. Thin section photomicrographs of dolomitised microbialitic carbonates from the autochthonous member

A, B – peloidal fabrics with some possible filaments in transmitted light, parallel polars (A) and CL (B). Dolomicritic peloids (yellowish or orange in CL) are bordered with microsparitic calcite (reddish in CL). Empty pore space is occluded with anhydrite (white in TL and dark in CL); transmitted light, parallel polars; sample 6. **C** – clotted fabrics with densely packed peloids rimmed with microsparitic calcite; sample 6. **D** – peloids forming carbonate stromatolitic laminae within gypsum (now anhydrite) stromatolite; larger oval peloids could be interpreted as fecal pellets, transmitted light, crossed polars; sample 8. **E, F** – numerous elongated peloids (fecal pellets or filaments?), transmitted light, crossed (E) and parallel polars (F); sample 15

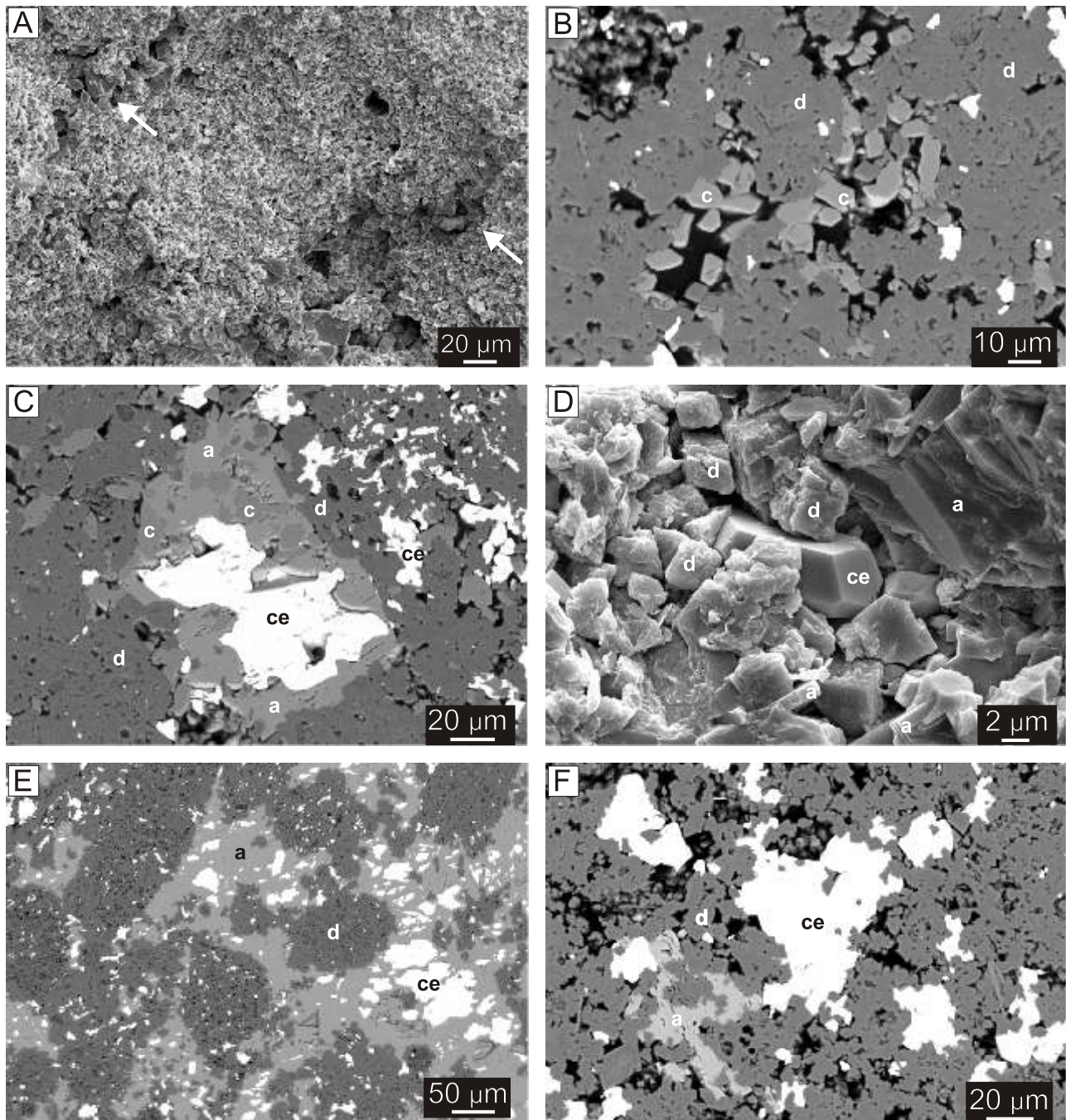


Fig. 7. SEM images of thin sections and fractured rock surfaces of the dolomitised microbialitic carbonates from the autochthonous member

A – peloidal clotted fabrics in microbialite; dolomitic peloids are rimmed with coarser microsparitic calcite cements (arrows); **B** – calcite cement (c) in the pores between small dolomitic peloids (d), white patches – celestite, black areas – pores; backscattered SEM image; **C** – mineral paragenesis typical of the carbonates studied with dolomite (d), anhydrite (a), calcite (c) and celestite (ce); **D** – dolomiticrite (d) with euhedral celestite crystal (ce) and anhydrite (a); **E** – cross-sections of elongated peloids composed of dolomiticrite (d) with high intercrystalline porosity, embedded within anhydrite cement (a) with abundant celestite (ce); backscattered SEM image; **F** – dolomite crystals with high intercrystalline porosity with anhydrite (a) and celestite (ce), dolomite (d); backscattered SEM image; A–C – sample 6; D – sample 8; E, F – sample 15

tain numerous anhydrite laths (Figs. 5D and 8A–E) and, strikingly, many silt-sized quartz grains, and feldspar and glauconite grains (Fig. 8C–E) but neither bioclasts nor microfauna. Only traces of calcite were detected in backscattered SEM images (Fig. 8E).

GEOCHEMISTRY

Oxygen and carbon isotopic ratios both in dolomite and in calcite are variable. The $\delta^{18}\text{O}$ values range from *ca.* –6 to +3‰ VPDB and the range of $\delta^{13}\text{C}$ values is from *ca.* –15 to +2‰ VPDB. Three isotopically separate groups of samples can be

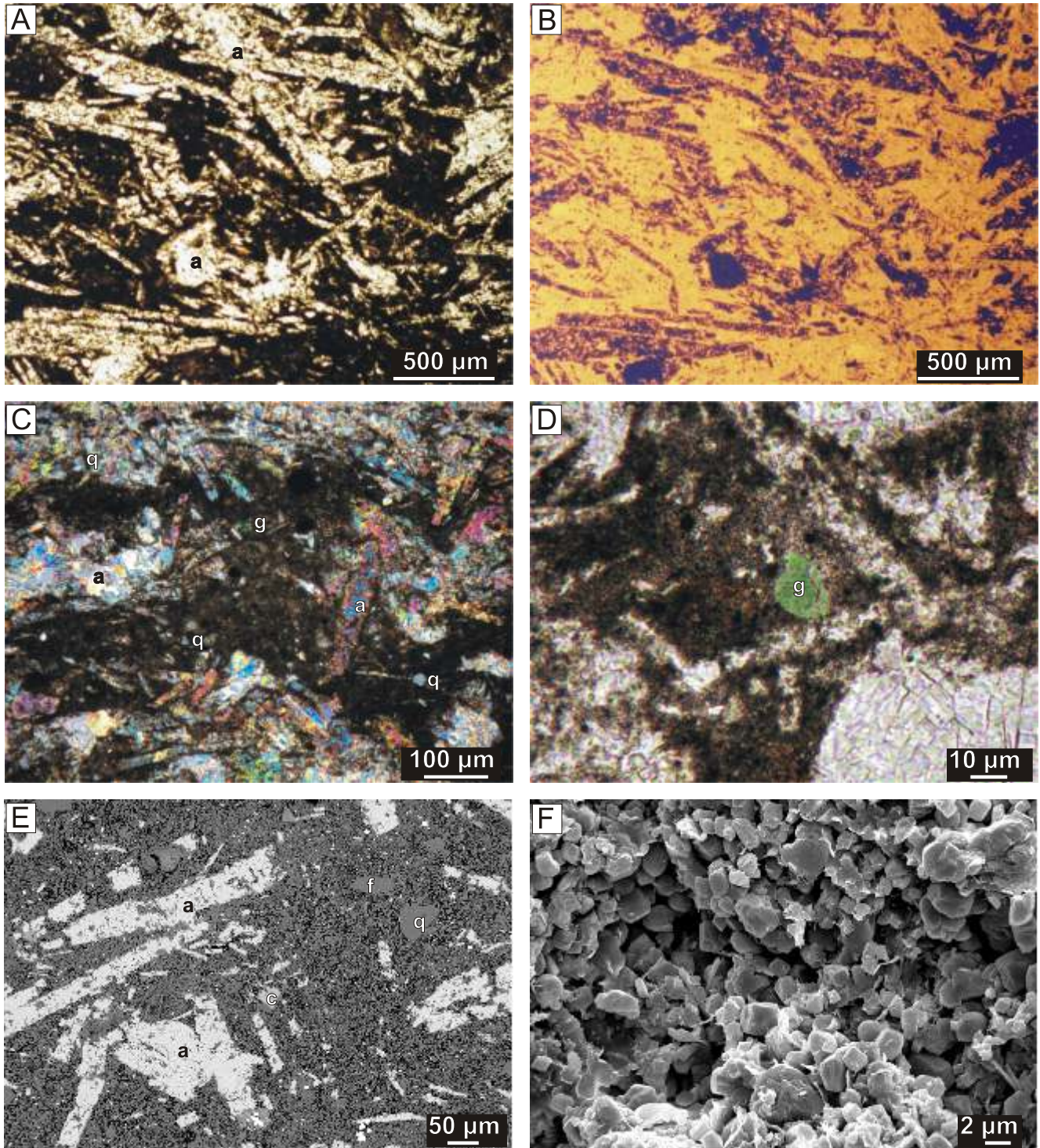


Fig. 8. Carbonates in the laminated anhydrite, sample 39

A, B – dolomite laminae (dolomite orange in B) with numerous anhydrite laths (a); **A** – transmitted light photomicrograph, parallel polars dolomite; **B** – CL; **C** – dense dolomicrite with anhydrite (a) laths or nodules and abundant terrigenous material, q – detrital quartz grains, g – glauconite grain, transmitted light photomicrograph, crossed polars; **D** – close-up of glauconite grain (g), transmitted light photomicrograph, parallel polars; **E** – dolomite lamina with anhydrite laths (a) and abundant terrigenous material (q – quartz, f – feldspar, c – calcite (?detrital grain), notice very high intercrystalline porosity; backscattered SEM image; **F** – highly porous dolomicrite constituting carbonate laminae, SEM image of fractured surface

distinguished; their δ -values are shown in various colours (white, grey or black) in [Figure 9](#).

There are two distinct groups of carbonates in the autochthonous member in terms of carbon and oxygen iso-

topes. The group occurring in the lower part of the member (samples 1–4), where the carbonate volume is negligible, is characterized by positive $\delta^{13}\text{C}$ signatures (average +1.7‰ VPDB in calcite and +1.8‰ VPDB in dolomite) and moder-

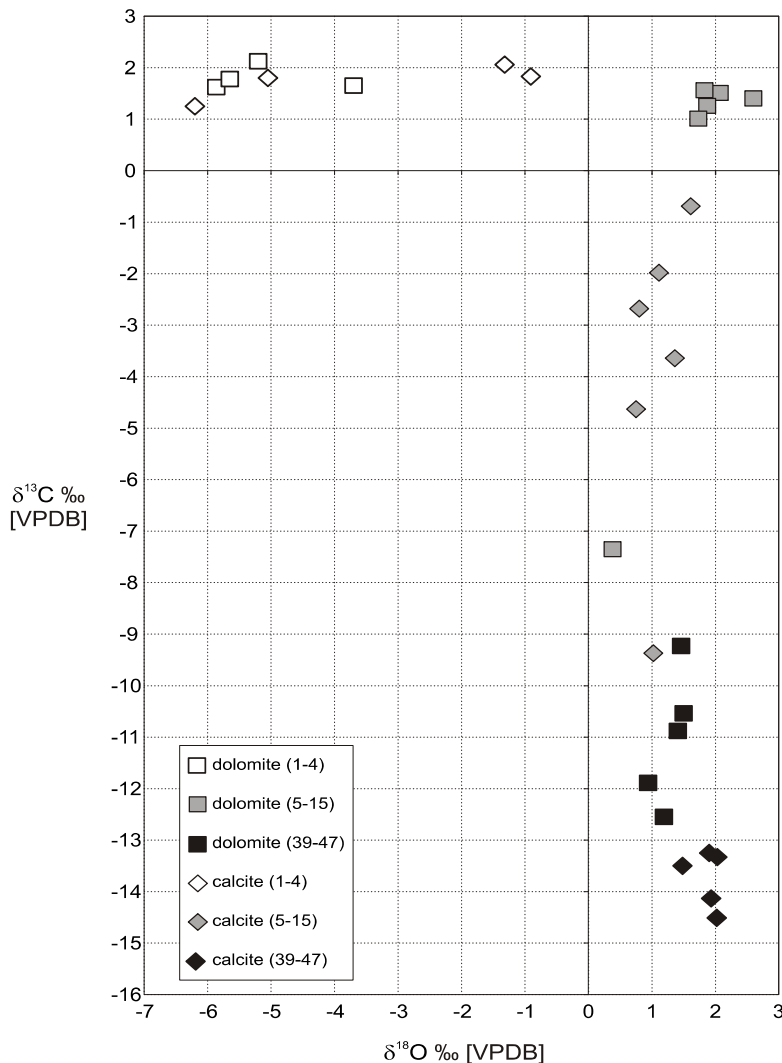


Fig. 9. Plot of $\delta^{18}\text{O}$ vs $\delta^{13}\text{C}$ values (‰ VPDB) for carbonates from the Wola Ró aniecka 7 section

ately negative $\delta^{18}\text{O}$ values (average -3.4‰ VPDB in calcite and -5.1‰ VPDB in dolomite). In turn, the group occurring in the upper part of the autochthonous member (samples, 5–8, 12, 15) records lower $\delta^{13}\text{C}$ values and higher $\delta^{18}\text{O}$ values. The mean $\delta^{13}\text{C}$ value of this group is -3.8‰ VPDB in calcite and $+1.4\text{‰}$ VPDB in dolomite (sample 6 was excluded from that calculation as it showed anomalous, isotopically very light values). The $\delta^{18}\text{O}$ values of this group are slightly positive both in calcite (average 1.1‰ VPDB) and in dolomite (average $+1.8\text{‰}$ VPDB; Fig. 9).

The carbonates in the allochthonous member record low $\delta^{13}\text{C}$ values which imply a significant contribution of organic carbon. The $\delta^{13}\text{C}$ values in dolomite range from -12.6 to -9.2‰ ; the average value is -11.0‰ VPDB. The $\delta^{18}\text{O}$ values of dolomite are similar to those in the second group of carbonates of the autochthonous member, and the average $\delta^{18}\text{O}$ value is 1.3‰ VPDB. The $\delta^{18}\text{O}$ signatures in calcite are slightly higher (average $+1.9\text{‰}$ VPDB) and the $\delta^{13}\text{C}$ values are significantly lower (average -13.7‰ VPDB) than in the dolomite.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in three anhydrite samples of the Wola Ró aniecka 7 borehole range from 0.71058 in sample 6 to 0.71947 in sample 1 (Table 1 and Fig. 2). The range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in five carbonate samples is much smaller (from 0.71024 in sample 43 to 0.71148 in sample 15; the average is 0.71059 ± 0.00051 – Fig. 2 and Table 1). In one sample (no. 6) Sr isotope values for carbonate and sulphate have been measured and it appeared that they differ only slightly (0.71059 for sulphate and 0.71039 for carbonate).

INTERPRETATION AND DISCUSSION

We interpret the carbonates occurring within the anhydrite section as having originated in the same sedimentary environment in which the sulphate deposits have accumulated. This environment was controlled by seawater, continental water eventually recycling previously deposited evaporites, and underground water as indicated earlier by several lines of geochemical evidence (e.g., Liszkowski, 1989; Petrichenko *et al.*, 1997; Eastoe and Peryt, 1999; Cendón *et al.*, 2004). A previous sulphur and oxygen isotope study of twenty anhydrite samples from the Wola Ró aniecka 7 borehole showed a range of $\delta^{18}\text{O}$ values from 12.4 to 16.4‰ (average $13.7 \pm 1.0\text{‰}$) and a range of $\delta^{34}\text{S}$ values from 21.9 to 25.7‰ (average $23.4 \pm 1.1\text{‰}$; Fig. 2), and in most cases both the $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ are higher than the contemporaneous marine values (Peryt *et al.*, 2002; Fig. 10). The recorded great spread of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values in the Badenian sulphates (Fig. 9B) was interpreted as due to the recycling of previously formed evaporites, already during gypsum precipitation in the Carpathian Foredeep Basin (Peryt *et al.*, 2002). However, the high $\delta^{34}\text{S}$ values

of the sulphate minerals as recorded in the Wola Ró aniecka 7 borehole could have resulted from isotope fractionation during microbially mediated reduction of SO_4^{2-} to S^{2-} bearing species: if sulphate reduction takes place in a closed basin setting, the residual dissolved SO_4^{2-} would have a higher $\delta^{34}\text{S}$ value than the original seawater (Utrilla *et al.*, 1992; Palmer *et al.*, 2004).

$^{87}\text{Sr}/^{86}\text{Sr}$ values of anhydrite (0.71058–0.71947) and carbonates (0.71024–0.71148) in the Wola Ró aniecka 7 borehole are much higher than the values of the contemporaneous Badenian seawater (e.g., McArthur *et al.*, 2001; Fig. 2). The onset of Badenian evaporite deposition in the Polish Carpathian Foredeep is dated at 13.81 ± 0.8 Ma based on $^{40}\text{Ar}/^{39}\text{Ar}$ dating of volcanic tuffs below the Badenian salts in Southern Poland (de Leeuw *et al.*, 2010). Assuming that the maximum duration of evaporite deposition was 600,000 years (de Leeuw *et al.*, 2010) and taking into consideration the upper and lower confidence limits (McArthur *et al.*, 2001), the global oceanic $^{87}\text{Sr}/^{86}\text{Sr}$ values would range from 0.708797 and 0.708816. The departures of the Sr-isotope values of anhydrites and carbonates of the Wola Ró aniecka 7 borehole indicate strong modifi-

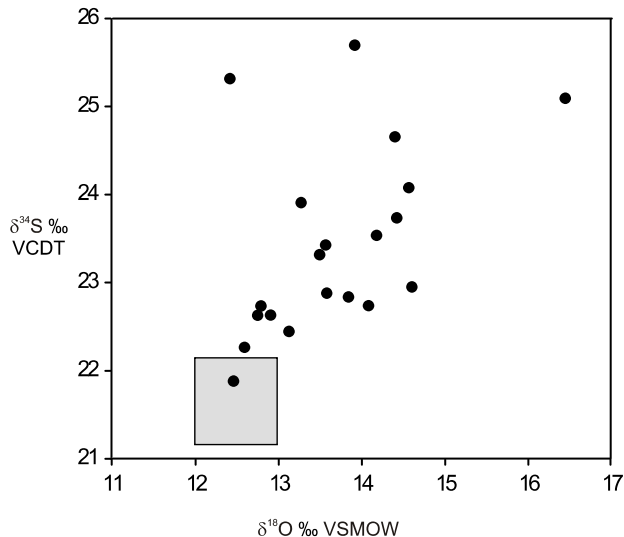


Fig. 10. Plot of $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values in the anhydrite from the Wola Ró aniecka 7 borehole (data after Peryt *et al.*, 2002)

The box shows the range of values for Miocene gypsum deposited from normal marine brines (after Paytan *et al.*, 1998 and Zak *et al.*, 1980)

of seawater-derived brines by highly radiogenic continental waters (*cf.* Kasprzyk *et al.*, 2007; Peryt *et al.*, 2010).

The $\delta^{18}\text{O}$ in the carbonate precipitates is dependent on the oxygen isotope composition of the water in which they were formed and the temperature of precipitation (Anderson and Arthur, 1983). The $\delta^{13}\text{C}$ of total dissolved carbon in any given water mass is a function of several factors which include the amount of CO_2 contributed by: organic matter degradation (with $\delta^{13}\text{C}$ values around -25‰ VPDB), dissolution of pre-existing carbonate rocks (usually $+1$ to $+2\text{‰}$), involvement of atmospheric CO_2 (-6 to -7‰) as well the extent of equilibration of atmospheric CO_2 with water masses ($+1$ to $+2\text{‰}$ at about 25°C) and the extent of photosynthetic withdrawal of ^{12}C into organic matter from the water mass (Anderson and Arthur, 1983).

Dolomites associated with evaporites are commonly interpreted as products of dolomitisation related to evaporitic fluids with high $\delta^{18}\text{O}$ values (reflux and sabkha models – e.g., Machel, 2004). The small dolomite bodies embedded within gypsum (now anhydrite) deposits in the Wola Ró aniecka 7 section could be related to hypersaline fluids with a high $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio originated due to gypsum precipitation which resulted in the removal of the Ca^{2+} ions from the brine.

Most dolomites in the autochthonous part of the section can be interpreted as products of microbially induced precipitation and/or dolomitisation. The dolomites exhibit peloidal clotted microfabrics typical of microbialites. Dolomite precipitation within microbial mats has been observed in many evaporitic environments such as Lagoa Vermelha in Brasil (Vasconcelos and McKenzie, 1997), lakes in the Coorong Lagoon area in Australia (Wright and Wacey, 2005) and in the Abu Dhabi sabkha in the Arabian/Persian Gulf (Bontognali *et al.*, 2010). It was also shown in experimental studies that microbial mediation is the only known mechanism to precipitate dolomite under earth surface conditions in both anoxic as well

aerobic environments (e.g., Vasconcelos *et al.*, 1995; Warthmann *et al.*, 2000; van Lith *et al.*, 2003; Sanchez-Raomán *et al.*, 2008), although certainly the experimental results do not apply to all cases.

The dolomites in the laminated anhydrite of the upper part of the Wola Ró aniecka 7 section do not show microbial microfabrics and probably have a different origin than microbially induced precipitation: they may be related to dolomitisation of carbonate mud by evaporitic hypersaline fluids in the early diagenetic/shallow burial environment.

A precise estimation of the dolomite precipitation temperature (or oxygen isotopic composition of water) is difficult not only because of the unknown oxygen composition of water (or temperature) but also because of the uncertainty about the fractionation factor between dolomite and the parental fluids (see Vasconcelos *et al.*, 2005; Wacey *et al.*, 2007). Recent studies have shown that at low temperatures the water-dolomite fractionation factor is much lower than at high temperatures (Vasconcelos *et al.*, 2005). The equation for the low temperature microbially mediated sedimentary dolomite given by Vasconcelos *et al.* (2005) produces visibly different results if it is compared to the usually used equation for high-temperature dolomites by Friedman and O'Neil (1977) (see Fig. 11A, B). In the case studied the equation for the low temperature dolomites should be applied. Rather low $\delta^{18}\text{O}$ values ($+1$ to $+2\text{‰}$ VPDB) in the dolomites studied indicate precipitation at relatively high temperatures. For example, if an arbitrary $\delta^{18}\text{O}$ value of water as high as $+4$ SMOW is assumed, then the dolomite precipitation temperature should fall somewhere near 40°C (see Fig. 11A). The assumption of a higher $\delta^{18}\text{O}$ value of water would result in much higher temperatures of dolomitisation which seems to be unrealistic. Strong depletion in the heavier oxygen isotope in the dolomite of the lowermost part of the autochthonous member ($\delta^{18}\text{O}$ values as low as -6‰ VPDB – Table 1 and Fig. 2) could be explained by diagenetic alteration related to higher temperatures in a deeper burial environment (see Fig. 11).

The presence of calcite cements in the upper part of the autochthonous member which postdate dolomite reflects possible changes in chemistry and in temperature of the pore fluids after the dolomitisation process. The calcite with $\delta^{18}\text{O}$ signatures similar to those of the dolomite had to precipitate from water either of significantly lower temperature or that was isotopically heavier than in the case of the dolomite (Fig. 11). The $\delta^{18}\text{O}$ value of calcite is 2.6‰ lower than coexisting dolomite if both minerals precipitated in isotopic equilibrium at the same temperature from the same solution (Vasconcelos *et al.*, 2005). When using the equation for high-temperature dolomites the discrepancy is even much larger ($4\text{--}7\text{‰}$ – see Vasconcelos *et al.*, 2005). As a decrease in temperature seems to be rather unrealistic during the progress of diagenesis, then the enrichment in the heavy oxygen isotope should be explained by another mechanism. Anhydritization and consequently expulsion of hydration water with a higher content of the heavy oxygen isotope into pore space might be one such mechanism causing in the increase in the $\delta^{18}\text{O}$ of pore fluids. Gypsum hydration water is enriched by *ca.* 4‰ compared to the water from which it precipitates (Gonfiantini and Fontes, 1963). In turn, the calcites

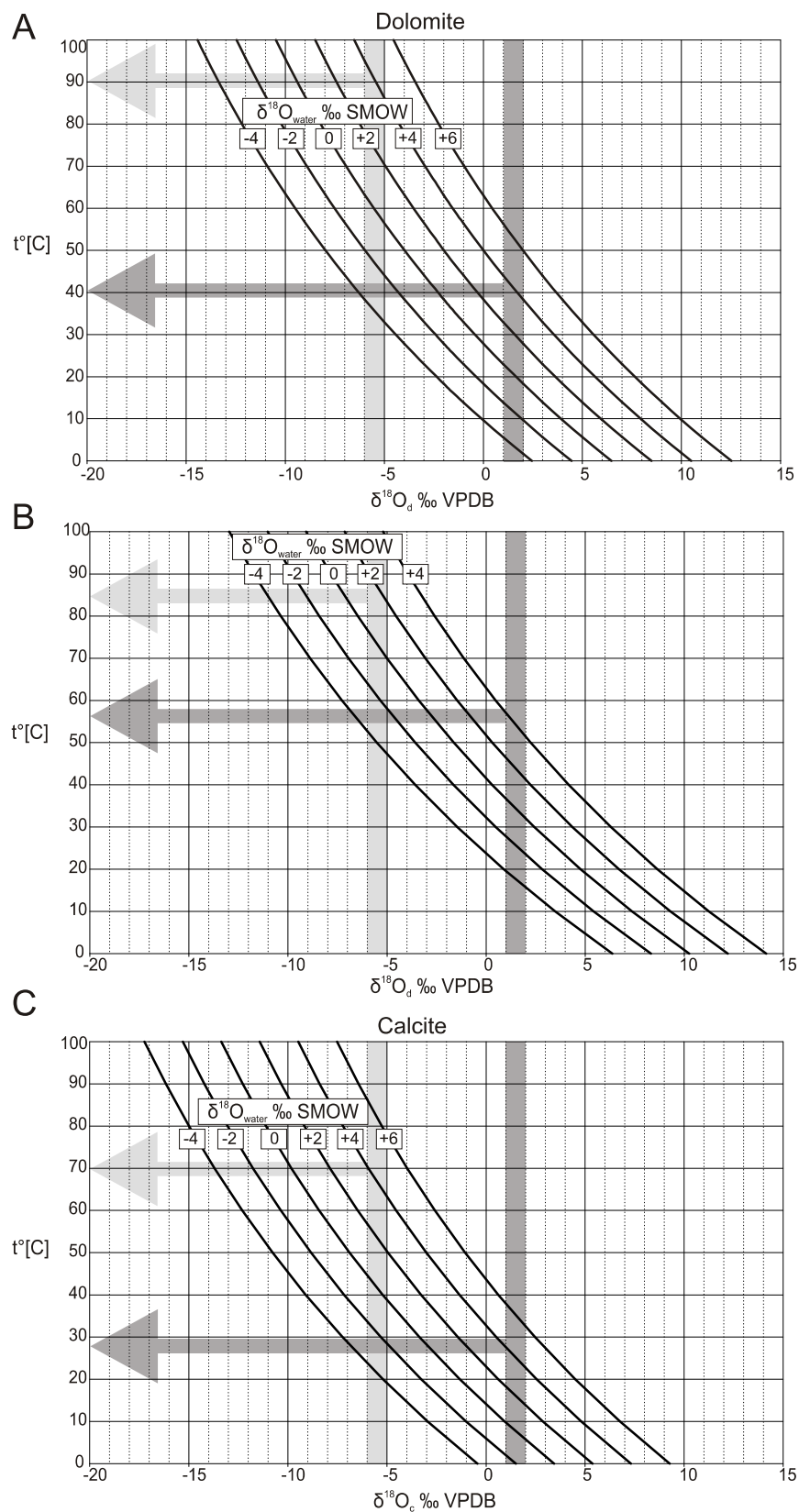


Fig. 11. Relationship between precipitation temperature and oxygen isotopic composition of water for dolomites (A, B) and calcites (C) according to equations given respectively by Vasconcelos *et al.* (2005) and Friedman and O'Neil (1977) for low- (A) and high-temperature (B) dolomites: $1000 \ln \alpha_{\text{dolomite-water}} = 2.73 \times 10^6 T^{-2} + 0.26$ and $1000 \ln \alpha_{\text{dolomite-water}} = 3.2 \times 10^6 T^{-2} + 1.5$ as well by Friedman and O'Neil (1977) for calcite (C): $1000 \ln \alpha_{\text{calcite-water}} = 2.78 \times 10^6 T^{-2} - 2.89$, and its interpretation for the Wola Ró aniecka 7 section. Grey-colored vertical bars refer to $\delta^{18}O$ values measured in dolomite and calcite, arrows mean possible precipitation temperatures at assumed oxygen isotopic composition of water

depleted in heavier oxygen from the lower part of the autochthonous member had to precipitate either at significantly higher temperatures or from presumably ascending water with lower $\delta^{18}\text{O}$ values, or possibly due to a combination of both factors.

The carbonates studied precipitated in water with variable contributions of dissolved inorganic carbon originated due to organic matter decomposition. During the diagenesis of carbonate deposits the carbon is usually a conservative element that does not change its isotopic composition very much (e.g., Banner and Hanson, 1990) and thus it can serve as a palaeoenvironmental proxy. Generally, the carbonates from the allochthonous member contain much more carbon of organic origin than those from the autochthonous member. Such divergence in the carbon isotope composition in carbonates of both intervals is evidence for different origins of the carbonate ions in the water from which they have precipitated.

The carbonates from the autochthonous member are mainly microbial precipitates that originated in a shallow subaqueous environment. Although some samples analysed contain carbonate ions originated due to organic matter oxidation, it seems that generally water was not very distant from equilibrium with atmospheric carbon dioxide. A similar phenomenon was observed in the case of the recent microbial dolomites forming in the evaporitic lakes in the Coorong area (Wacey *et al.*, 2007). The $\delta^{13}\text{C}$ values of the calcium carbonate laminae within the allochthonous member are very depleted in the heavier carbon isotope and thus they unquestionably indicate a very significant contribution of carbonate derived from organic matter decomposition. The locus and the mechanisms of precipitation of those carbonates seem to be rather ambiguous. On the one hand, the carbon isotopic signature clearly suggests water with a high content of carbon dioxide of organic origin. Such enrichment could take place in aerobic and, subsequently, in possibly anaerobic conditions associated with sulphate bacterial reduction (e.g., Pierre, 1989), within a stratified and poorly mixed brine body. On the other hand, the carbonate intercalations containing extrabasinal terrigenous siliciclastic material could have precipitated due to new surface water inputs into the basin.

As previously mentioned, the bacterial reduction of sulphate ions in the bottom water might account also for the observed higher $\delta^{34}\text{S}$ values in the allochthonous member than in the autochthonous member (Fig. 2) as, during organic matter decomposition, sulphate-reducing bacteria preferentially utilize lighter sulphate ions enriching the remaining fraction in heavier isotopes (e.g., Kaplan, 1983). On the other hand, reducing conditions should eventually lead to dissolution of gypsum deposited at the basin bottom as in the Dead Sea bottom sediments (see Warren, 1989, p. 141) which is not the case, at least in the section studied. Moreover, the carbonates and associated anhydrite clearly do not show any evidence of being deposited in anaerobic conditions. The carbonates are light in colour (whitish or beige) and do not contain e.g. pyrite or organic matter, which is indicative of oxygenated water. Therefore, it seems that the carbonates of the allochthonous member in the Wola R6 aniecka 7 section have precipitated and deposited in an aerobic environment.

The sedimentological characteristics of the allochthonous member indicate that the carbonates have been deposited from suspension. The carbonates precipitated somewhere in the surface waters or in the water column and definitely not at the bottom. They formed distinct laminae within laminated allochthonous gypsum (now converted to anhydrite) mainly of turbidite origin (*cf.* Kasprzyk and Ortí, 1998; Peryt, 2000). Carbonate intercalations are probably related to the water inputs that caused supersaturation with respect to calcium carbonate. Mixing of the water with brine with a high content of organic carbonate could be responsible for calcium carbonate precipitation. It seems that the presence of the dispersed clastic material is unambiguously associated with the calcium carbonate precipitation, so the waters that transported the clastics into the basin at the same time triggered the precipitation of calcium carbonate.

CONCLUSIONS

The geochemical study of carbonates and sulphates occurring within the Badenian anhydrite section of the Wola R6 aniecka 7 (SE Poland) supports earlier concepts (based on lithofacies and geochemical studies of the sulphates) advocating the important role played by continental waters during the deposition of the allochthonous evaporites in the Carpathian Foredeep Basin. In addition, this study indicates that the continental waters have been the controlling factor also during the deposition of the autochthonous evaporites. These waters were highly radiogenic during the evaporite deposition as indicated by $^{87}\text{Sr}/^{86}\text{Sr}$ values of anhydrite (0.71058–0.71947) and carbonates (0.71024–0.71148) that are much higher than the values of the contemporaneous Badenian seawater. In most cases both the $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of anhydrite are higher than the contemporaneous marine values due to the recycling of gypsum.

The dolomites of the autochthonous member exhibit peloidal clotted microfabrics typical of microbialites. These microbially-precipitated dolomites formed in a salina environment. The dolomite of the upper, allochthonous member has a different origin: the carbonate mud precipitated chemically due to mixing of brine with river water in the marginal part of the basin, was resedimented toward the basin centre, and then dolomitised. Oxygen isotope signatures are practically identical in the upper part of the autochthonous member and in the allochthonous member (average +1.1 and +1.9‰ VPDB in calcite and +1.8 and +1.3‰ VPDB in dolomite, respectively) because the dolomitising fluid in both cases was a chemically similar brine at the stage of gypsum deposition. Carbon isotope signatures are different in the upper part of the autochthonous member and the allochthonous member (average –3.8 and –13.7‰ VPDB in calcite and +1.4 and –11.0‰ VPDB in dolomite, respectively) due to variable contributions of organic carbon. The deposition of the autochthonous member took place in a very shallow subaqueous environment, in water not very distant from equilibrium with atmospheric carbon dioxide, and the organic carbon contribution was small. In the allochthonous member that originated mostly in the

deeper, probably stratified, basin, carbon from organic matter oxidation dominated in the pool of carbonate ions.

Rather low $\delta^{18}\text{O}$ values in the studied dolomites indicate precipitation at relatively high temperatures *ca.* 40°C where a $\delta^{18}\text{O}$ value of water = +4 SMOW is assumed, and a depletion in the heavier oxygen isotope in the dolomite of the lowermost part of the autochthonous member is explained by diagenetic alteration related to higher temperatures in a deeper burial environment. The presence of calcite cements in the upper part of the autochthonous member which postdate dolomitisation re-

flects possible changes in the chemistry and temperature of the pore fluids after the dolomitisation process.

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