Geologica Acta, Vol.10, N° 4, December 2012, 319-332
DOI: 10.1344/105.000001753
Available online at www.geologica-acta.com

geologica acta

Carbon and oxygen isotopic composition of the Middle Miocene Badenian gypsum-associated limestones of West Ukraine

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ABSTRACT

The middle Miocene Badenian basin of the Carpathian Foredeep is characterized by complex sedimentary and diagenetic carbonate-evaporite transitions. Six locations have been selected to evaluate the controls on the carbon and oxygen isotopic composition of the Badenian gypsum-associated limestones of the Tyras Formation in West Ukraine. At three locations marine limestones overlie the gypsum, at one location (Anadoly) the gypsum-associated limestones are polygenic, and at two localities (Pyshchatyntsi and Lozyna) gypsum deposits are lacking. The studied limestones have originated as primary, mostly peloidal carbonates as well as secondary carbonates formed by hypogene sulphate calcitisation. They show a wide range of $\delta^{13}C$ (from from -0.9‰ to -39.8‰) and $\delta^{18}O$ values (from 0.9‰ to -12.2‰). The Badenian limestones formed in marine environments (either as deposits accumulated at the bottom of the sea or forming the infillings of solution cavities within gypsum) have less negative $\delta^{18}O$ values compared to predominantly diagenetic formations. Wide ranges and usually very negative $\delta^{13}C$ values and low $\delta^{18}O$ values of those limestones indicate that they suffered important meteoric diagenesis as supported by common sparitic fabrics. In addition, a large range of $\delta^{13}C$ values even in the group of samples characterized by less-negative $\delta^{18}O$ values shows that bacterial sulphate reduction and methane oxidation were active processes in the pore fluids of the Tyras Formation. Very low carbon isotopic compositions ($\delta^{13}C$ values from -22 to -40‰) of some sparitic limestones in the studied sections indicate the occurrence of oxidized methane within the diagenetic environment. Accordingly, the isotopic signatures of the studied limestones are a combination of both primary and secondary processes, the latter having a primordial importance. The common occurrence of similar negative $\delta^{13}C$ and $\delta^{18}O$ values in evaporite-related carbonates in other Miocene evaporite basins suggest that extensive dissolution-reprecipitation in diagenetic or vadose-phreatic environments were common in evaporite-related carbonates.

KEYWORDS **Middle Miocene. Ukraine. Sedimentology. Limestones. Stable isotopes. Gypsum.**

INTRODUCTION

Carbonates and evaporites are commonly lateral equivalents, both in carbonate-dominated environments or within the evaporite basins themselves. They may be accompanied by diagenetic transitions when chemical changes in the fluids cause dissolution of unstable mineralogy and replacement by minerals which are stable under the new chemical conditions (Rouchy *et al.*, 2001). This complex picture is characteristic of some Miocene evaporite basins of the Mediterranean and Paratethys areas where large bodies of diagenetic carbonates are found replacing sulphate deposits (often co-occurring with sulphur deposits) (*e.g.*, Decima *et al.*, 1988; Jassim *et al.*, 1999; Pawlowski *et al.*, 1979; Pierre and Rouchy, 1988).

A carbon and oxygen isotope study may supply important information on variations of the ambient parameters (temperature and geochemistry of the diagenetic fluids) at the time of carbonate crystallization (Pierre and Rouchy, 1988) and thus it is an important tool for palaeoenvironmental analysis (Armstrong-Altrin *et al.*, 2009, with references herein). The previous studies on the middle Miocene Badenian gypsum-associated limestones in West Ukraine have shown a very wide range of $\delta^{13}C$ values (Vinogradov *et al.*, 1961; Lein *et al.*, 1977; Peryt and Peryt, 1994) and a wide range (from +1‰ to -11‰) of $\delta^{18}O$ values (Peryt and Peryt, 1994). The aim of this paper is to discuss the controls on carbon and oxygen isotopic composition of the gypsum-associated limestones from six localities in the Ukrainian part of the Carpathian Foredeep basin: Lozyna, Pidpechery, Zvenyachyn, Optymistychna Cave, Pyshchatyntsi and Anadoly (Fig. 1). These limestones are in various facies and show diversified lateral and vertical relations regarding the gypsum deposits (Fig. 2).

GEOLOGICAL SETTING

The Carpathian Foredeep basin, filled mostly by Middle Miocene deposits, is the largest foredeep basin in Europe as it stretches for more than 1300km from the environs of Vienna to the NW part of Bulgaria (Oszczypko *et al.*, 2006). In the outer zone of the Ukrainian part of the Carpathian Fore-

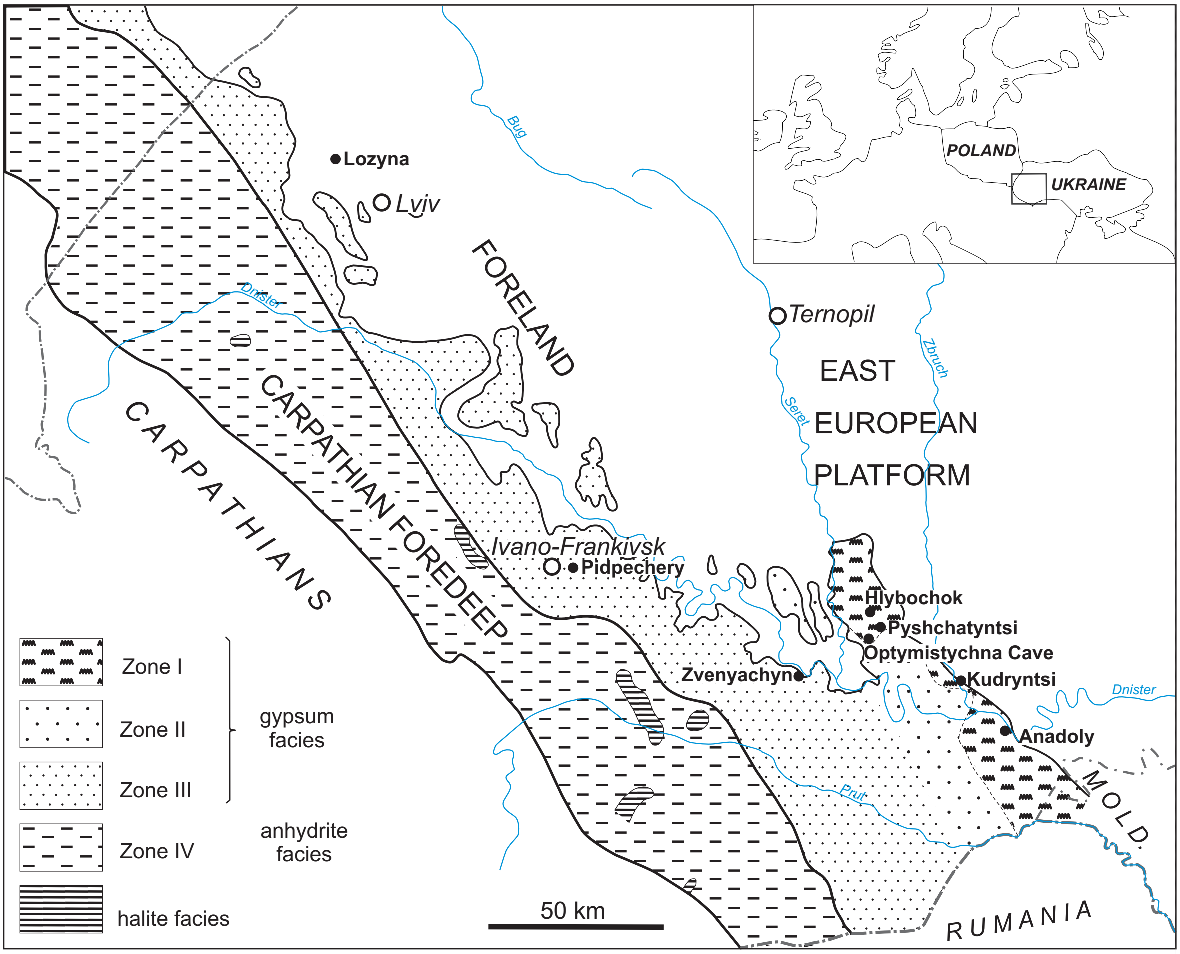

FIGURE 1 | Location map, showing the studied localities and the facies zones of the Badenian sulphate rocks (after Peryt, 2006a).

deep and the foreland, the section of middle Miocene deposits is clearly tripartite with marine siliciclastics and carbonates several tens to several hundreds of meters thick below the Badenian evaporites, and marine to brackish siliciclastic deposits up to 5km thick above the Badenian evaporites (Vjalov *et al.*, 1981; Oszczypko *et al.*, 2006). During the late Badenian, evaporites (sulphates and more rarely halite) accumulated in the outer part of the foredeep. In addition, gypsum has been deposited in a part of the foreland where it commonly overlies the Mesozoic or Paleozoic substrate or lower Badenian sandy or coralline algal limestones (Kudrin, 1966; Oszczypko *et al.*, 2006). The sedimentology of this gypsum has been studied by Peryt (2001, 2006a, with references herein), Petrichenko *et al.* (1997) and Bąbel (2007, with references herein). Three main zones of gypsum development occur in the peripheral parts of the basin (Peryt, 2001; Fig. 1). Zone I consists entirely of stromatolitic gypsum formed in a nearshore zone. Zone II is located more basinward and is characterized by stromatolitic gypsum in the lower part of the section, overlain by a sabre gypsum unit. Zone III occurs in still more basinward areas and is characterised by giant gypsum intergrowths in the lowermost part, overlain by stromatolitic gypsum, sabre gypsum and then by clastic gypsum units. Correlation between these facies and zones was achieved using lithological marker beds and surfaces (Peryt, 2001).

Our studied localities come from all those gypsum zones. Anadoly, Pyshchatyntsi, and Optymistychna Cave are located within Zone I, Zvenyachyn within the field of Zone II, and Pidpechery in Zone III (Fig. 1). Lozyna in turn is placed outside the present limit of gypsum, although gypsum does occur west and southwest of Lviv in Zone III (Peryt, 1996, 2001).

The gypsum is commonly overlain by massive, very dense, often cavernous limestones (a few tens of centimetres to a few metres thick) which have been termed “supra-gypsum limestones”, even if gypsum deposits were lacking, until Łomnicki (1897) introduced the term “Ratyn Limestone” for those deposits. It is commonly accepted that the sedimentation of the Ratyn Limestone was preceded by weathering, karstification and erosion of the earlier deposited gypsum (Aleksenko, 1961; Bobrovnik, 1966; Koltun *et al.*, 1972; Peryt and Peryt, 1994).

Study of the stratotype section of Ratyn Limestone at Ratyn Mount (eastern part of Lviv) indicated that there are peloidal and more rare intraclastic limestones showing mudstone and wackestone depositional textures with bioclasts (bivalves, gastropods, foraminifers). Those limestones are underlain by recrystallised, barren limestones with pseudomorphs after gypsum crystals (Venglinskiy and Goretskiy, 1979; Peryt, 2006b), often porous and cellular and described as formed at the expense of gypsum (Nowak, 1938; Teisseyre, 1938; Kudrin, 1955). The term Ratyn Limestone has been applied also to barren limestones overlying sulfur-bearing limestones (Koltun, 1965). In recent cartographic syntheses (*e.g.* Gerasimov *et al.*, 2005; Vashchenko *et al.*, 2007), two main types of carbonate facies have been distinguished in the Ukraine: metasomatic sulfur-bearing limestones (epigenetic limestones) and pelitic limestones of evaporitic origin, *i.e.* the Ratyn Limestone (Kudrin, 1955, 1966; Polkunov, 1990; Klimchouk, 1997). The latter group is regarded as primary-sedimentary (*e.g.* Gerasimov *et al.*, 2005). Among this group, Peryt and Peryt (1994) distinguished the marine facies of the Ratyn Limestone which are characterized by the presence of marine fauna (for fauna inventory, see Kudrin, 1955, 1966; and Venglinskiy and Goretskiy, 1979), and we follow this distinction.

The Badenian evaporites and the Ratyn Limestone are included in the Tyras Formation (Petryczenko *et al.*, 1994; Andreyeva-Grigorovich *et al.*, 1997) which is overlain by deep-marine Kosiv Formation in the Carpathian Foredeep and the adjacent part of the foreland as well as by various marine facies in more marginal parts of the basin (Table 1); their origin is related to the general late Badenian transgression.

The Tyras Formation dips 1° to 3° towards the foredeep. In hydrogeologic terms, the lower part of the Kosiv Formation and the Ratyn Limestone form the original upper aquifer, and the lower Badenian sandstones and limestones form the lower aquifer. The role of the gypsum has changed with time, from initially being an aquiclude to a karstified aquifer, and the major part of the foreland of the Carpathian Foreland is the zone of entrenched gypsum karst (Klimchouk and Aksem, 2001).

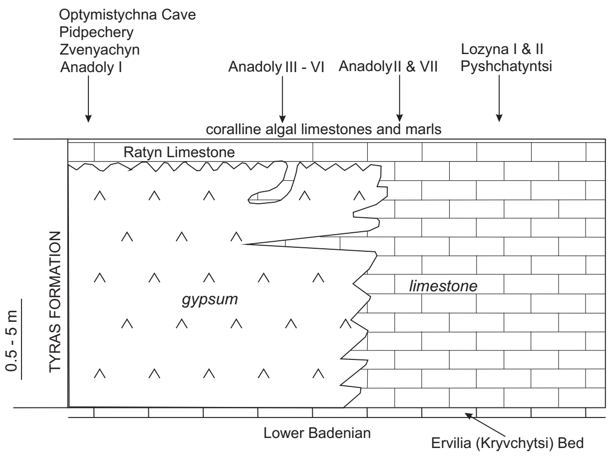

FIGURE 2 | Diagrammatic picture of the development of the Tyras Formation in the marginal zone of the Carpathian Foredeep Basin showing the inferred position of studied localities.

TABLE 1 | Middle Miocene stratigraphy of the Ukrainian Foredeep Basin

Global stages	Paratethys stages	Local units	Deposits
Serravallian	lower Sarmatian	Dashava formation	Siliciclastic deposits
	upper Badenian	Kosiv formation	Siliciclastic deposits in the basin, accompanied by coralline algal limestones in the marginal zone
		Tyras formation	Sulphates and halite (in the basin center); in the marginal zone the gypsum is overlain by Ratyn Limestone
Langhian	lower Badenian	Marine siliciclastics and coralline algal limestones [locally Ervilia (Kryvchytsi) Bed at the top]	

In the Optymistychna Cave, Pidpechery and Zvenyachyn, the Ratyn Limestone (usually a few tens of centimetres thick) shows peloidal packstone/wackestone textures and overlies various levels of the gypsum sequence (Peryt, 1996; Bąbel, 2005). Anadoly (in the geological literature also known as Darabany) belongs to classical localities of the Tyras Formation, with a long tradition of study of the Ratyn Limestone (*e.g.* Sidorenko, 1904; Vyrzhikovskiy, 1925; Koltun *et al.*, 1972). There is a number of outcrops (mostly abandoned quarries) of gypsum covered by the Ratyn Limestone (usually 1.2–1.8m thick) and then by rhodoid-bearing marls with limestone intercalations at Anadoly. In addition, limestones occur also within gypsum as well as in places where gypsum deposits are lacking, and in the latter case they overlie the older Badenian strata (*cf.* Prysjazhnjuk, 1998; Fig. 1). For the purpose of this paper, the key outcrops are designated by Latin numbers (I–VII) and their GPS data are given in Table I (Electronic Appendix, available at www.geologica-acta.com). A clay layer of a few centimetres of thickness very often occurs at the boundary between the Ratyn Limestone and the gypsum at Anadoly, followed by a celestite-bearing bed (Sidorenko, 1904; Koltun *et al.*, 1972).

Thin stromatolitic gypsum (4m in thickness) is exposed at the limits of Hlybochok village in the Drapaka River valley (Klimchouk and Aksem, 2001) and is overlain by the Ratyn Limestone (3m thick), mostly peloidal and peloidal-intraclastic packstones and grainstones, and sometimes microbial-peloidal rocks. About 250m further down the valley the gypsum disappears and *ca.* 3km down the valley the Ratyn Limestone attains a thickness of 6m in Pyshchatyntsi.

There is a number of natural exposures of the Ratyn Limestone in the environs of Lozyna as well as one sandpit (Lozyna I section) where the Ratyn Limestone (3.5m thick) overlies the Lower Badenian deposits (Wysocka, 2002). In the Lozyna I section the limestone is mostly peloidal-intraclastic packstone/grainstone and sparitic; it shows a denser appearance in the northern part of the outcrop and is more brecciated in the southern part. The outcrop Lozyna III is located *ca.* 1km SE of Lozyna I and the Ratyn Limestone (of a total thickness of 7.0m), is overlying cross-bedded sandstones. It contains intercalations of bedded mudstones containing clasts of rocks showing calcite pseudomorphs after gypsum crystals as well as other varieties of the Ratyn Limestone.

MATERIAL AND METHODS

Four localities of marine facies of the Ratyn Limestone overlying gypsum deposits have been selected for isotopic study: Optymistychna Cave, Pidpechery, Zvenyachyn and Anadoly I (Figs. 1, 2). The Ratyn Limestone is usually peloidal packstone/wackestone, and sometimes intraclastic with bioclasts (bivalves, gastropods, foraminifers, ostracods, echinoids) (Figs. 3A, B); in Anadoly I, in addition, peloidal-intraclastic-ooidal grainstones and packstones occur (Peryt and Peryt, 1994, fig. 3), and sparitic limestones form the celestite bed.

Primary depositional facies of the Ratyn Limestone can also be recognized in Anadoly IV where an erosional pocket in gypsum, some 2m above the outcrop base, is filled by bedded fine-grained sandstone and peloidal limestone. In Anadoly V, furrows, pipes and caves originated due to gypsum dissolution (Fig. 4A) and are located one meter or more below the base of the laminated gypsum unit. The cavities contain irregular limestone bodies (usually several centimetres thick) composed of mostly bioclastic-peloidal-intraclastic packstones with fine quartz grains and laminated peloidal rocks, as well as fragments of gypsum crystals (Fig. 4D). The bioclasts include echinoids, rhodoids, foraminifers, brachiopods and ostracods (Figs. 4B, C). In Anadoly VI, furrows in gypsum are filled by laminated fine-grained sandstone accompanied by discontinued lenticular limestones - often peloidal packstones, sometimes with relict microbial laminae; in addition to peloids, intraclasts (up to 1cm), fine quartz grains, ooids and bioclasts (ostracods, gastropods, foraminifers, shell fragments occur) (Figs. 4E, F).

Other outcrops in Anadoly are mostly composed of diagenetic facies of limestone. These are sparitic limestone with peloidal, possibly microbial discontinuous laminae and micritic cement portions aligned along former gypsum crystals, now filled by blocky calcite cement (Fig. 3D), 1.1m (Anadoly III) – 3.2m (Anadoly VII) thick. At the top the limestone is brecciated and numerous generations of sparite fillings of veins occur. However, in the various portions of the unit (at the base in Anadoly II, in the middle in Anadoly III, and in their lower and middle parts in Anadoly VII) depositional facies can be distinguished – these are peloidal deposits (Fig. 3C) with rare bioclasts (foraminifers, ostracods and shell fragments). In Anadoly VII, located *ca.* 100m from the nearest gypsum outcrop, a characteristic bed (25cm thick, Fig. 4G) consisting of veins and portions of sparite that occur in bedded peloidal rock showing microbial relics and rare ostracods, builds the limestone basal part. The overlying lower part of the Ratyn Limestone shows brecciation, with many generations of calcite veins, and is composed of sparite and microsparite containing relics of microbial lamination and rare pseudomorphs after gypsum crystals at the top.

In the Drapaka River valley we have studied two outcrops (Pyshchatyntsi and Hlybochok, Fig. 2) where only diagenetic facies of the Ratyn Limestone were observed. At the base of the unit in Pyshchatyntsi, bedded peloidal packstone with fine pseudomorphs after gypsum crystals occurs, and it is covered by brecciated micrite and microsparite with peloidal parts and pseudomorphs after gypsum crystals (Fig. 4H). The upper part of the unit is made up of peloidal packstones-grainstones with intraclasts or portions with very fine pseudomorphs after gypsum crystals. In the Hlybochook outcrop located close to the gypsum limit, the Ratyn Limestone is sparitic with microbial portions and relics after gypsum crystals.

In the Lozyna I (Figs. 2, 5A) and Lozyna II sections, the diagenetic facies are superimposed on the depositional carbonate facies. The limestone is mostly peloidal-intraclastic packstone/grainstone with rare bioclasts (Fig. 5B, C), and in Lozyna I it is accompanied by sparite (which shows peloids and microbial relics), with intraclasts attaining a few centimetres in size, some of them with calcite pseudomorphs after gypsum crystals. Porous sparite and microsparite with relict microbial lamination and locally laminated mudstones (sometimes with quartz grains) occur in the upper part of the unit in the Lozyna III outcrop.

The isotopic analyses of limestones were performed in the Mass Spectrometry Laboratory at Maria Curie-Skłodowska

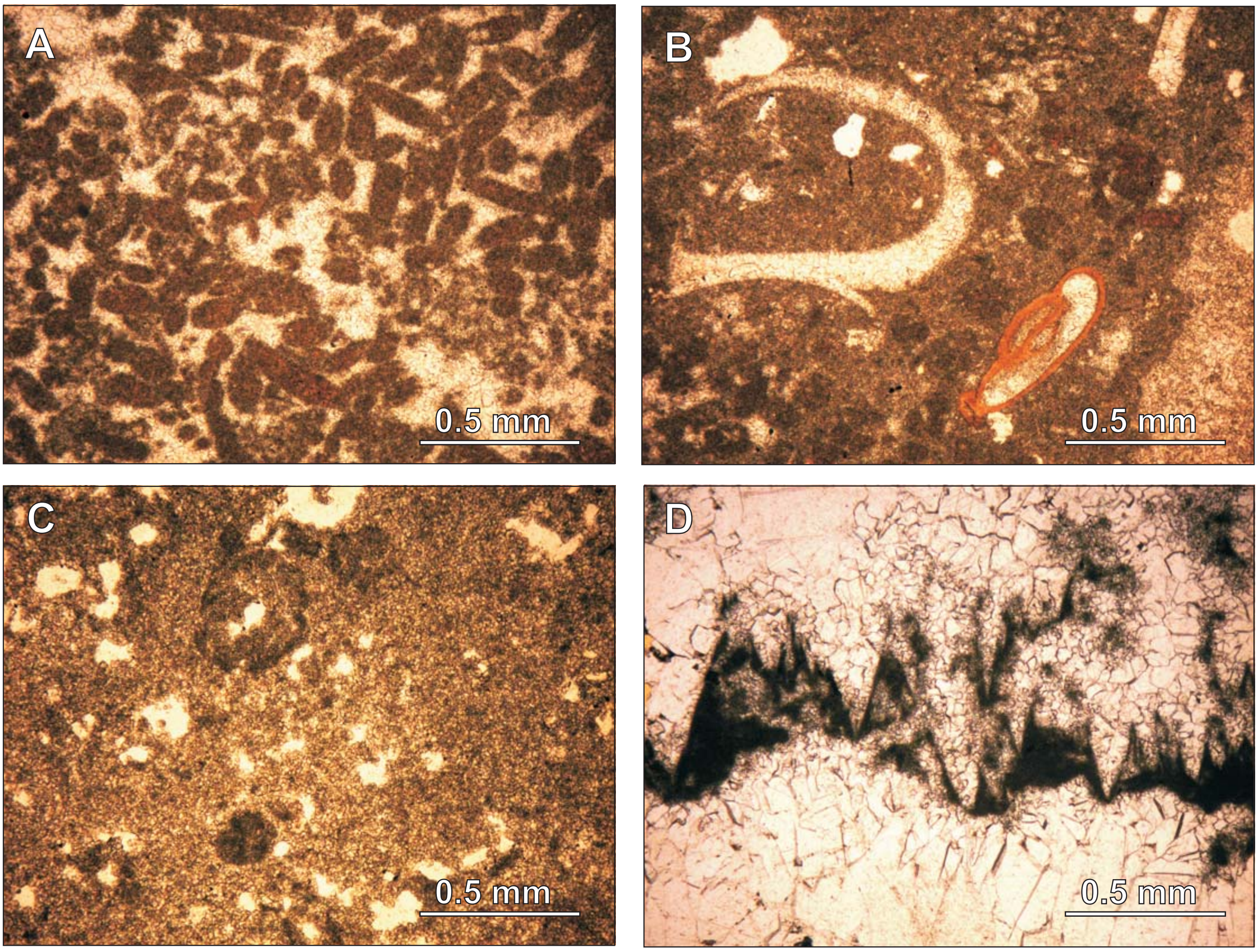

FIGURE 3 | A) Pelsparite containing abundant pellets of unknown but possibly fecal origin, Zvenyachyn; B) Bioclasts (gastropods and foraminifers) and peloids within the micritic matrix that is recrystallised in some places (lower right corner), Optymistychna Cave; C) recrystallised peloidal wackestone, Anadoly II; D) terminations of calcitised gypsum crystals within the sparry cement, Anadoly II.

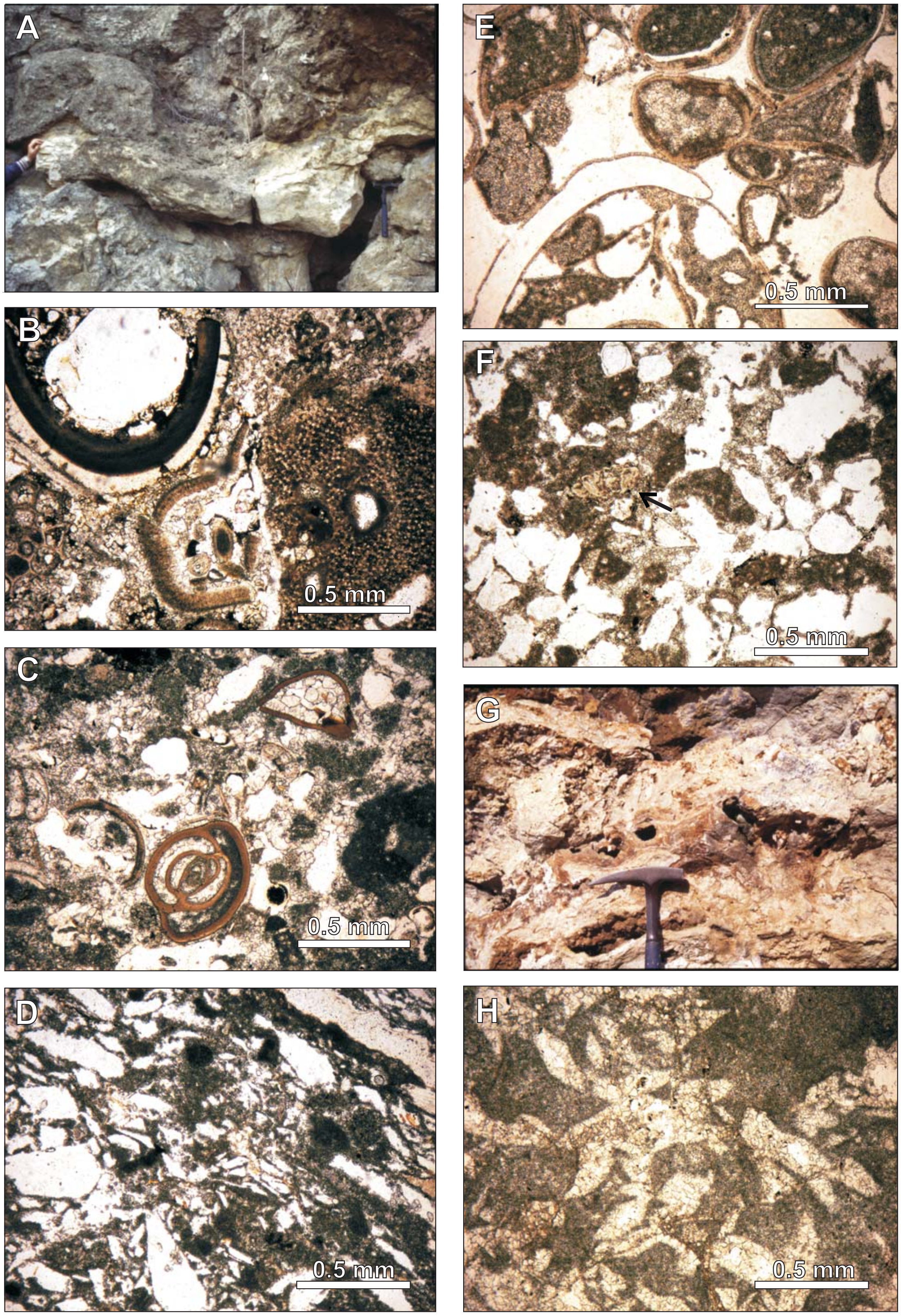

FIGURE 4 | A-D) Irregular limestone body within A) gypsum in Anadoly outcrop V, indicated by a hand (left) and a hammer (right). The limestone often shows B, C) bioclast packstone texture, with common B) echinoderms, B) bivalves and C) foraminifers, and in places common D) fragments of gypsum crystals occur; E) Ooid grainstone with bivalve mould coated by micrite envelope, Anadoly outcrop VI; F) Foraminifer (arrow) and other carbonate grains (possibly skeletal) within fine-grained quartz sandstone filling pockets within gypsum, Anadoly outcrop VI; G) Basal bed of Anadoly outcrop VII; H) Calcite pseudomorphs after lenticular gypsum crystals, Pyshchatyntsi.

University in Lublin, Poland. Either hand-picked specimens or slabbed specimens (with other slabs used to produce standard thin sections) have been sampled selectively. A 1.5mm diameter stainless steel drill with tungsten carbide coating was used for material extraction from the surfaces of the specimens. CO_2 gas was extracted from the samples by reaction of calcite with H_3PO_4 (McCrea, 1950) at 25ºC in a vacuum line, following the standard preparation procedure. The gas was purified of H_2O on a P_2O_5 trap and collected on a cold finger. Isotopic compositions were analyzed using a modified MI1305 triple-collector mass spectrometer equipped with a gas ion source. Isobaric correction was applied. After subsequent normalization to measured certified reference materials, the isotopic composition was expressed in per mille (‰) relative to the Vienna Pee Dee Belemnite (VPDB) international standard. Analytical precision of both $\delta^{13}C$ and $\delta^{18}O$ in a sample was ±0.08‰. In total, 72 new samples of gypsum-associated limestones have been analysed. The only carbonate mineral recognized in the analyzed sample set was calcite.

Considering the diameter of the drill sample (1.5mm) and the petrographic variability shown by the studied rocks (Figs. 3-5), the isotopic sampling has to be regarded as whole rock analysis. Consequently, each resulting isotopic measurement would reflect both depositional and diagenetic fluids, particularly when spar phases abound or are common (such samples are included into a group showing sparitic fabric). The samples where spar phases are lacking are included into a group showing non-sparitic fabric (Table I).

RESULTS

The results of the isotopic study are shown in Table I and in the plot of isotope data. The sparitic fabric and non-sparitic fabrics are differentiated based on the earlier petrographic examination of samples (Fig. 6). Significant correlation was only found for non-sparitic samples, from which linear regression parameters are given in Table 2. Analysis for the sparitic fabric samples revealed no significant correlation coefficient (r<0.2) between $\delta^{13}C$ and $\delta^{18}O$ values. Average $\delta^{13}C$ and $\delta^{18}O$ values of most outcrops are given in Table 3.

The $\delta^{13}C$ and $\delta^{18}O$ values of the Ratyn Limestone samples representing the primary marine facies (i.e. from Optymistychna Cave, Pidpechery and Zvenyachyn) are within the range of -3.5 to -8.5‰ and -1.1 to -2.6‰, respectively (Table I), which are characteristic for the marine facies of the region (Table 4). Primary depositional facies of Anadoly IV – VI (Table I) show similar $\delta^{13}C$ values (the range from 0.9 to -10.6‰, with most of the values contained between -3.8 and -7.4‰) while the $\delta^{18}O$ values (0.5 to -5.2‰) are mostly slightly depleted compared to the data reported above.

The $\delta^{13}C$ and $\delta^{18}O$ values of diagenetic facies of the Ratyn Limestone show a large spread of data and in general are strongly negative (Table I, 3, Fig. 6) although a wide dispersion of $\delta^{13}C$ and $\delta^{18}O$ values (Table I, Fig. 6) is not random, as indicated by a general good correlation of $\delta^{13}C$ and $\delta^{18}O$ values. There are two distinct groups of $\delta^{13}C$ and $\delta^{18}O$ values which can be distinguished in particular outcrops, although not necessarily in the same stratigraphic order (cf. Lozyna and Pyshchatynsti): the first group is characterized

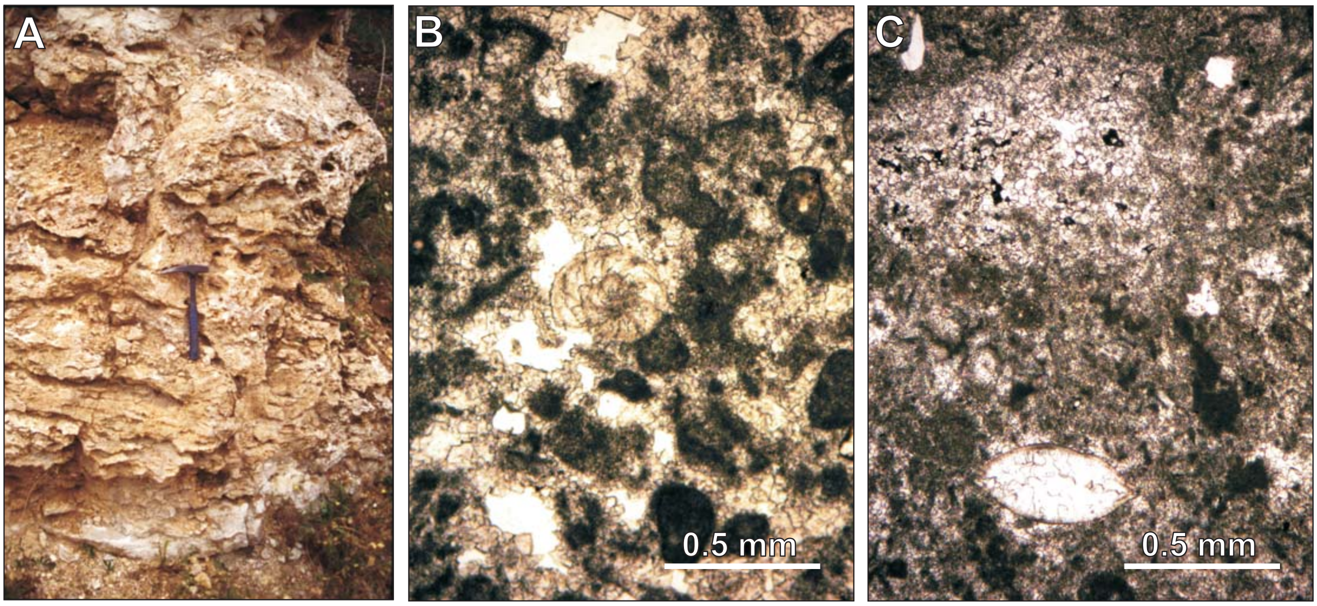

FIGURE 5 | A) Lower part of the Lozyna I outcrop, showing common brecciation and vugs; B) Foraminifer in peloidal-intraclastic wackestone/packstone, Lozyna I; C) Ostracod in peloidal, partly recrystallised, wackestone/packstone, Lozyna III.

by less negative $\delta^{13}C$ and $\delta^{18}O$ values, and the second one by clearly more negative $\delta^{13}C$ and $\delta^{18}O$ values. In most cases, this grouping overlaps with the sparitic and the non-sparitic fabric groups (Fig. 6). In a few cases (Anadoly II, base; Anadoly III, top) the $\delta^{13}C$ and $\delta^{18}O$ values of diagenetic facies are exceptionally high (Table I) although petrographically they do not differ much from the adjacent limestones.

INTERPRETATION

Gypsum-associated limestones in the Badenian of the Ukrainian Carpathian Foredeep and the foreland include a

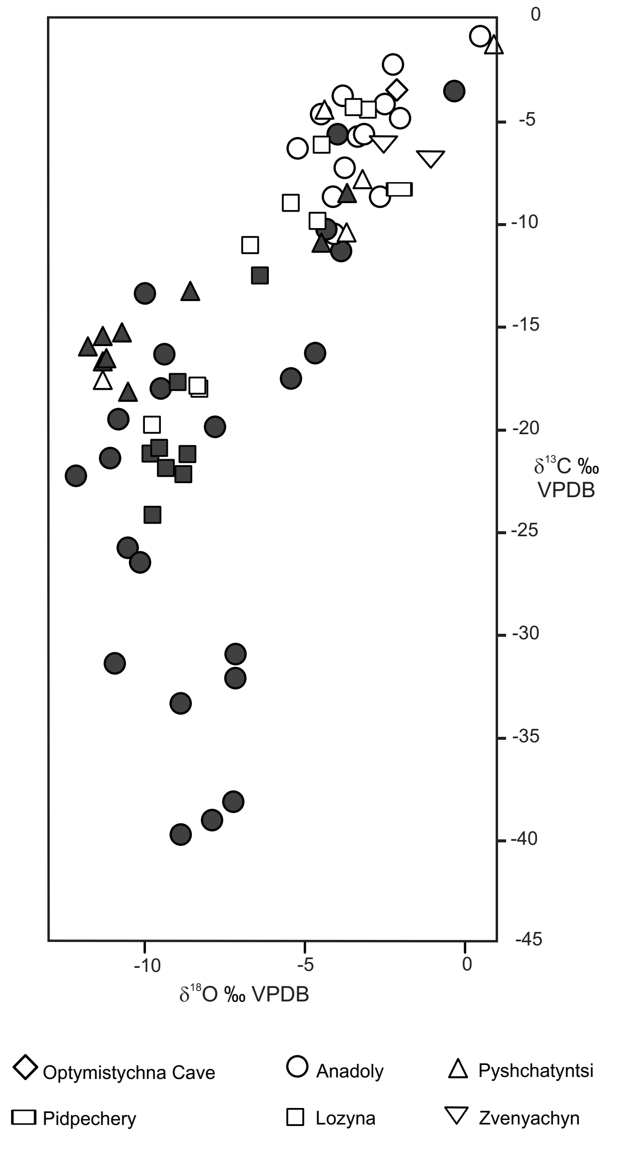

FIGURE 6 | Plot of $\delta^{13}C$ and $\delta^{18}O$ values of Badenian gypsum-associated limestones of West Ukraine: empty symbols show non-sparitic fabrics and filled symbols show sparitic fabrics (see Table 2 for linear regression data).

mixture of primary and gypsum-replacement textures, and the isotope data and petrographic observations are consistent with the presence of: i) one or more primary (marine) phases; ii) distinct meteoric diagenetic phases and iii) the presence of oxidized methane within the diagenetic environment. An intensive epigenetic imprint masks the effects of syngenetic carbonate formation in evaporative settings such as lagoons that have existed during the initial stage of late Badenian transgression into the Carpathian Foredeep evaporite basin, and thus the meteoric diagenetic phase is volumetrically the most important.

A primary marine phase is recorded in Optymistychna Cave, Pidpechery, Zvenyachyn, Anadoly V and VI and is characterized by peloidal packstones with bioclasts and intraclasts, and more rare peloidal grainstones and wackestones; in addition, ooidal grainstones occur in Anadoly VI. These carbonates show the $\delta^{13}C$ values range from -10.6 to 0.9‰ and the $\delta^{18}O$ values vary from -5.2 to 0.5‰. The earlier reported data for the marine facies of the Ratyn Limestone in Anadoly I (Peryt and Peryt, 1994) fit those ranges well except for the basal celestite-bearing bed (sample 118, Table I) which is more depleted in ^{13}C and slightly depleted in ^{18}O. The $\delta^{13}C$ and $\delta^{18}O$ values for one sample from Anadoly IV are characteristic of the marine Ratyn Limestone, but there are sparite portions in the rock that indicate the presence of a meteoric diagenetic phase in the sample.

In addition, there are samples of peloidal deposits lacking sparitic fabrics and showing relatively high $\delta^{13}C$ and $\delta^{18}O$ values which are interpreted as inherited after primary evaporative limestone in Anadoly II (basal sample), Anadoly III (top sample), Lozyna I (base of the section) and in various parts of Lozyna III and Pyshchatyntsi sections (Table I).

The meteoric diagenetic phase is characterised by the occurrence of sparitic fabric and, first of all, calcite pseudomorphs after gypsum crystals, as well as by lower $\delta^{18}O$ values (commonly <-10‰) than those recorded in the primary marine facies, and a great range of $\delta^{13}C$ values (Pyshchatyntsi, Hlybochok, Anadoly II, Anadoly VII, Table I). The calcitisation of gypsum (and anhydrite) within such limestones was a hypogene process (Stafford *et al.*, 2008) and the sulphate minerals have been replaced by calcite spar as gravity-driven meteoric waters passed downdip (*cf.* Scholle *et al.*, 1992).

The distribution of $\delta^{13}C$ and $\delta^{18}O$ values in the Anadoly VII and Pyshchatyntsi sections of the Ratyn Limestone is bipartite (Fig. 7, Table 3). This may reflect the polyphase nature of meteoric diagenesis and/or various reducing agents (organic matter, crude oil, and methane) which controlled the microbial sulphate reduction in particular parts

TABLE 2 | Linear regression data for studied samples (na: not applicable)

Outcrop	Slope	R	Constant	N
All samples	1.91±0.19	0.75	-2.24±1.33	72
All (without samples showing $\delta^{13}C$ values ≤30‰)	1.65±0.10	0.88	-2.09±0.72	65
Samples showing non-sparitic fabric	1.60±0.17	0.87	-1.26±0.81	32
Samples showing sparitic fabric	na	no corr.	na	40
Anadoly (all samples)	2.49±0.39	0.73	-0.66±2.76	37
Anadoly (without samples showing $\delta^{13}C$ values ≤30‰)	1.89±0.18	0.89	-0.88±1.21	30
Anadoly (only samples showing $\delta^{13}C$ values ≤30‰)	na	no corr.	na	7
Pyshchatyntsi	1.16±0.12	0.94	-3.57±1.03	14
Lozyna	2.77±0.18	0.97	4.94±1.40	17

of the studied sections; as already stated, the Badenian gypsum-associated limestones in the Carpathian foreland include a mixture of primary and gypsum-replacement textures, and the proportion of the fractions fluctuates. The carbon sources are typified by distinct carbon isotopic compositions: methane is extremely depleted in ^{13}C, crude oil is less depleted ($\delta^{13}C$ values from -35 to -25‰), and marine organic matter tends to have $\delta^{13}C$ values of approximately -25 to -20‰ (see Ziegenbalg *et al.*, 2010, with references herein).

Occurrence of oxidized methane within the diagenetic environment is evidenced by low carbon isotopic composition of sparitic limestones of Anadoly III ($\delta^{13}C$ values from -39.8 to -31.5‰ except for the top sample, Table I). We assume also that Lozyna I outcrop documents the co-occurrence of brecciated zones and adjacent dense clusters indicating focused, ascending, hydrocarbon-rich fluids (*cf.* Stafford *et al.*, 2008). Except for samples of peloidal-intraclastic grainstone near the base of the outcrop which are characterized by less negative $\delta^{13}C$ (>-10‰) and $\delta^{18}O$ values (>-6‰), most of the other samples are characterized by more negative $\delta^{13}C$ and $\delta^{18}O$ values (*ca.* -22‰ and *ca.* -9.5‰, resp.) which form an almost flat line in the profile (Fig. 7). It should be mentioned, however, that there is a large lateral variation regarding the rock brecciation even in the lowermost part of the section. The former presence

TABLE 3 | Average values of $\delta^{13}C$ and $\delta^{18}O$

Outcrop	$\delta^{13}C$ [‰]	$\delta^{18}O$ [‰]
Anadoly II	-22.5±7.6	-9.6±1.6
Anadoly III	-35.7±3.7	-8.5±1.4
Anadoly IV and VI	-5.0±0.8(1)	-3.8±1.0(1)
Anadoly V	-8.1±2.1	-3.3±0.9
Anadoly VII	-18.0±4.9	-8.2±3.2
Pyshchatyntsi (total)	-11.9±5.2	-7.2±4.2
Pyshchatyntsi (lower part)	-14.6±3.8	-9.3±3.1
Pyshchatyntsi (upper part)	-8.6±2.9	-4.1±0.4
Lozyna I	-19.4±5.4	-9.0±1.9
Lozyna I(2)	-21.8±1.7(2)	-9.8±0.7(2)
Lozyna III	-10.7±6.1	-5.8±2.4
Sparitic fabrics	-20.2±8.7	-8.4±2.8
Non-sparitic fabrics	-8.0±5.1	-4.2±2.7

(1)Sample nº. 117 excluded
(2)Three samples from the basal part of the section excluded

of evaporites is indicated by (rare) occurrence of dedolomitization fabric and of intraclasts composed of calcite pseudomorphs after gypsum crystals (which are not very common). Highly porous limestones characterized by strongly negative $\delta^{13}C$ values probably record methane venting episodes in the Lozyna I outcrop. The methane source was biogenic methanogenesis taking place in the upper Badenian and Sarmatian strata of the Carpathian Foredeep (*cf.* Kubica, 1997).

DISCUSSION

Our data confirm the microbial origin of most limestones (*cf.* Table I). They also reveal that there were several episodes of alteration of sulphate deposits by meteoric waters. The first episode was related with the structural rebuilding of the Carpathian Foredeep when the gypsum deposits underwent subaerial exposure recorded in various parts of the basin (*e.g.* Aleksenko, 1961; Bobrovnik, 1966; Peryt and Peryt, 1994). The subsequent, more volumetrically important meteoric episodes are related to the uplift and erosion of the Carpathian Foredeep basin that commenced around 10.5Ma (Oszczypko *et al.*, 2006); those episodes of alteration by meteoric waters resulted in the common occurrence of calcites with low $\delta^{18}O$ values. Precipitation of such calcites results from the involvement of isotopically light fluids (such as meteoric waters), from formation at elevated temperatures, or a combination of both factors (Arthur *et al.*, 1983). Cross-plots of carbon and oxygen isotope values shows significant correlation and are characterized by the pronounced slopes seen in "mixing lines" (Table 2) produced by physical mixing of two phases with distinct isotope chemistry: a high $\delta^{13}C$ and $\delta^{18}O$ marine end member and a low $\delta^{13}C$ and $\delta^{18}O$ meteoric phase, as it is commonly envisaged in carbonate formations (*e.g.* Buonocunto *et al.*, 2002, fig. 6; Suarez *et al.*, 2009, fig. 5). A good part of the variability observed among samples could thus result from different mixing ratios of the two phases, and possibly also from many episodes of dissolution and reprecipitation, as it was envisaged for the Kudryntsi section (Peryt and Peryt, 2009). The deviations from the simple mixing between a saline seawater and a less saline, isotopically depleted fresh water, may have resulted from other factors (*e.g.* evaporation) influencing the stable isotope composition of the mixing components (Latal *et al.*, 2004, with references herein).

All diagenetic phases in the studied limestones have lower isotopic values than primary phases and in particular the sparry calcites have exceptionally low isotopic signatures which are far removed from seawater-derived components. If the extreme values of the $\delta^{18}O$ values are applied to solve Kim and O'Neil's equation (1997) for temperature of crystallization, an unrealistically high temperature

TABLE 4 | Average values for marine facies of the Ratyn Limestone (after Peryt and Peryt, 1994, fig. 5; please notice that there is an error in the explanation of isotope curves in Peryt and Peryt, 1994, fig. 3, where the $\delta^{13}C$ should run $\delta^{18}O$, and vice versa)

Locality	Number of analyses	$\delta^{13}C$ [‰]	$\delta^{18}O$ [‰]
Belogirka	2	-1.8	-1.4
Criva (Moldova)	4	-1.6	-4.7
Oleshiv, Palahychi	3	-5.0	-3.2
Pidkamin'	3	-3.1	-1.9
Plugiv	2	-4.7	-5.2
Ratyn Mount	4	-3.9	-3.5
Verenchanka	5	-4.8	-2.0

range results (Table 5). There is no geological evidence for either a substantial burial depth of the Badenian in the foreland area or high regional heat flow which would result in elevated temperature during diagenesis. Therefore the Badenian carbonates are interpreted to have undergone only shallow burial diagenesis. In addition, there is a considerable variation of $\delta^{18}O$ values in the same bed as indicated by Gąsiewicz (2000), which excludes the possibility of very different temperatures of isotopic restructuring. Pierre and Rouchy (1988) suggested that massive occurrences of diagenetic carbonates presenting anomalous low $\delta^{18}O$ values could originate during gypsum or anhydrite reduction by sulphate-reducing bacteria when large quantities of energy have been released, which led to the temperature increase in sediments even at shallow depths. Their conclusion could be supported by the lowest $\delta^{18}O$ values recorded in Anadoly outcrops II, III and VII, Pyshchatyntsi and Lozyna, but the general abundance of meteoric diagenesis seems to discount such a possibility.

Precipitation of calcites with low $\delta^{13}C$ values most commonly results from the incorporation of CO_2 from organic sources including soil zones with plant-derived gases, decomposition of disseminated organic matter or subsurface bacterial or thermogenic breakdown of hydrocarbons (Scholle *et al.*, 1992). A large range of $\delta^{13}C$ values even in the group of samples characterized by less-negative $\delta^{18}O$ values shows that methanogenesis was an active pro-cess in the pore fluids (Pierre and Rouchy, 1988). The variability of the carbon isotopic ratio of calcite spars is often interpreted to be the result of a localized distribution of oil accumulations as well as of the variable amounts of leakage or degradation of such hydrocarbons before cement formation (*e.g.* Scholle *et al.*, 1992). The samples with very negative $\delta^{13}C$ values (-22‰ to -40‰) reflect the introduction of carbon dioxide derived from oxidized methane, under both oxygenated and anoxic conditions such as the samples from Anadoly outcrop III where only the topmost

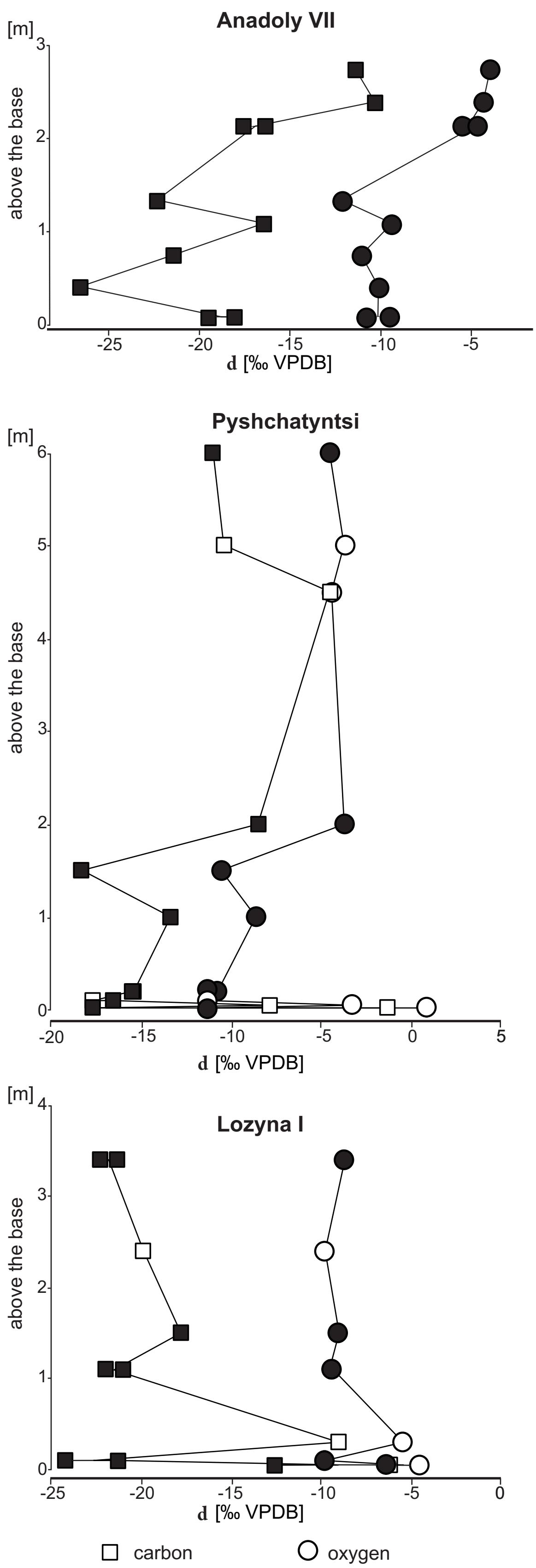

FIGURE 7 | Isotope profiles of Anadoly outcrop VII, Pyshchatyntsi and Lozyna I. Empty symbols show non-sparitic fabrics and filled symbols show sparitic fabrics.

TABLE 5 | Temperature ranges calculated after Kim and O'Neil (1997) assuming $\delta^{18}O$ value of water = 0‰

Locality	Outcrop	T [°C]
Optymistychna Cave		24.8
Pidpechery		24.8
Zvenyachyn		20.0-27.3
Anadoly	I	56.0
	II	25.3-75.2
	III	16.7-75.9
	IV	34.5
	V	24.3-35.0
	VI	12.5-41.0
	VII	34.5-85.0
Pyshchatyntsi		10.7-82.2
Lozyna	I	37.2-68.6
	III	29.3-59.7

sample examined shows marine nature (although modified in a meteoric environment) and the others show very negative $\delta^{13}C$ values (-31.5 to -39.8‰).

High variability of isotopic values is characteristic for modern and Holocene shallow water carbonate settings (absolute ranges of 6.9‰ for $\delta^{13}C$ and 5.5‰ for $\delta^{18}O$, Gischler *et al.*, 2009) where the strongest isotopic excursions are caused by diagenesis near subaerial exposure horizons (Gischler *et al.*, 2009). A wide dispersion of $\delta^{13}C$ and $\delta^{18}O$ values is also characteristic for many other carbonate formations, including other Miocene gypsum-related limestones (*e.g.* Decima *et al.*, 1988; Pierre and Rouchy, 1988; Montana *et al.*, 1994), and in particular the Badenian post-selenitic limestones (Gąsiewicz, 2000). A major difference between the isotopic characteristics of post-selenitic limestones characterized by Gąsiewicz (2000) on the one hand and the Ratyn Limestone on the other hand, is a variable pattern of $\delta^{13}C$ values (Fig. 8) and clearly lower average $\delta^{13}C$ value (-41.4‰) in post-selenitic limestones (Gąsiewicz, 2000).

As concluded by Montana *et al.* (1994), the lowest $\delta^{18}O$ and $\delta^{13}C$ values are measured in the samples of the Messinian Calcare di Base which showed extensive dissolution-reprecipitation evidences, while the samples having a relatively preserved micritic framework are characterized by more positive values. They interpreted this as due to exchange processes in a diagenetic or vadose-phreatic environment. The earlier interpretations (*e.g.* Decima *et al.*, 1988) assumed that the wide dispersion of the isotopic values was due to random syngenetic inputs of meteoric water in the depositional environment. Gąsiewicz (2000, fig. 23) recognized that the $\delta^{18}O$ values of cements in Badenian post-selenitic limestones are usually lower than those of matrix, and concluded that the cements could crystallize from meteoric waters (Gąsiewicz, 2000).

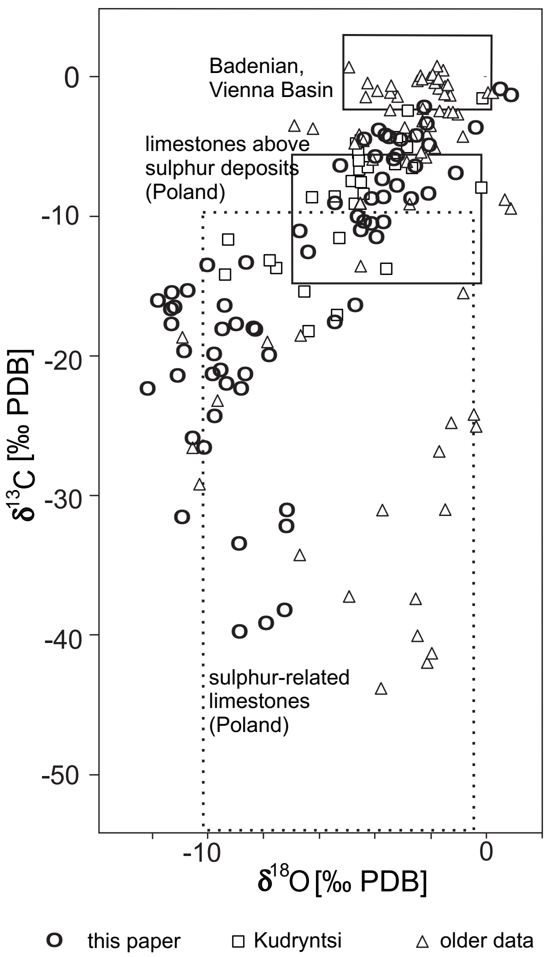

FIGURE 8 | Plot of $\delta^{13}C$ and $\delta^{18}O$ values of Badenian gypsum-associated limestones of West Ukraine, showing older data (Peryt and Peryt, 1994) and data on Kudryntsi section (Peryt and Peryt, 2009). Fields for sulphur-related limestones in Poland (after Gąsiewicz, 2000), limestones above sulphur deposits in Poland (after Pawlikowski and Przybyłowicz, 1979), and the Vienna Basin (after Kováčová et al., 2009) are also shown.

The concept relating negative $\delta^{13}C$ and $\delta^{18}O$ isotopic values recorded in the Badenian gypsum-associated limestones in West Ukraine with extensive dissolution-reprecipitation in a diagenetic or vadose-phreatic environment does not exclude the possibility that systematic pattern variation of the δ values may indeed indicate that this relationship was controlled by restriction to open-marine exchange – the more negative, the more restricted (*cf.* Kováčová *et al.*, 2009). However, if the geographic factor was of any importance in the differentiation of the $\delta^{13}C$ and $\delta^{18}O$ values of the Ratyn Limestone, subsequent diagenetic overprint has totally obscured any possible initial differentiation.

CONCLUSIONS

Limestones that are physically related to gypsum deposits in the Middle Miocene Badenian (Tyras Formation) of West Ukraine have originated as primary, mostly peloidal carbonates which underwent several episodes of alteration of sulphate deposits by meteoric waters. They show wide ranges of $\delta^{13}C$ and $\delta^{18}O$ values suggesting significant water-host rock interaction during the meteoric water flow, and the large range of $\delta^{13}C$ values, even in the group of samples characterized by less-negative $\delta^{18}O$ values, show that bacterial sulphate reduction and methane oxidation were active processes in the pore fluids of the Tyras formation. The Tyras limestones formed in marine environments (either as deposits accumulated at the bottom of the sea in shallow subtidal environments or forming the infillings of solution cavities within gypsum) are less negative compared to predominantly diagenetic formations. Wide ranges with usually very negative carbon and, especially, oxygen isotopic compositions of those limestones indicate that they suffered a significant meteoric diagenesis, a notion additionally supported by the presence of the common sparitic fabrics. However, in addition to the hypogene calcitisation of gypsum (and anhydrite) when gravity-driven meteoric waters passed downdip the Tyras formation, the changes of $\delta^{13}C$ and $\delta^{18}O$ values in particular parts of the studied sections indicate an important role of reducing agents which controlled the microbial sulphate reduction and methane oxidation processes, the latter being expressed by a very low carbon isotopic composition (*e.g.* $\delta^{13}C$ values from -39.8 to 31.5‰ in Anadoly III outcrop) of sparitic limestones. In some cases the rock brecciation, dedolomite fabric and intraclasts are composed of calcite pseudomorphs after gypsum crystals. All those features suggest the former presence of sulphate evaporites and are observed in highly porous limestones showing strongly negative $\delta^{13}C$ values (*ca.*-22 ‰ in Lozyna I outcrop); those limestones are interpreted as recording methane venting episodes. Similar isotopic values recorded in other cases of evaporite-related carbonates in the Carpathian Foredeep basin of Ukraine and Poland as well as in other middle and upper Miocene evaporite basins suggest common extensive dissolution-reprecipitation of such carbonates in diagenetic or vadose-phreatic environments.

ACKNOWLEDGMENTS

The fieldwork and geochemical analyses were supported by research grant Nº. 6 P04D 009 11 (Committee on Scientific Research) to T.M. Peryt and special grant Nº. UKRAINA/193/2006 (Ministry of Science and Higher Education) to M. Kotarba. We thank M. Jasionowski and I.I. Turchinov for the field assistance, to M. Bąbel, G. Czapowski, C. Pierre and in particular the journal editors for their comments and suggestions, and to Miles F. Beaux II for the final English check.

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Manuscript received February 2010;
revision accepted October 2011;
published Online January 2012.

ELECTRONIC APPENDIX

TABLE I | Stable isotope results of carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) of analysed bulk samples of middle Miocene Badenian gypsum- associated limestones of West Ukraine. Results for samples with non-sparitic fabric are shown in bold print

Locality	Outcrop number (and GPS data)	Sample number	$\delta^{13}C$ [‰]	$\delta^{18}O$ [‰]	Sample location	Description of limestone
Optymistychna Cave			**-3.5**	**-2.1**		peloidal-intraclast packstone (bivalves, gastropods, forams)
Pidpechery			**-8.4**	**-2.1**		porous peloidal packstone
Zvenyachyn		3.1	**-6.2**	**-2.6**		bioturbations? filled by peloidal grainstone in peloidal wackestone-packstone
		3.2	**-6.9**	**-1.1**		
Anadoly	I – N48°27.160’, E26°33.067’	118	-19.9	-7.8	celestite bed just below the Ratyn Limestone	
	II – N48°27.066’, E26°33.476’;	96-2	**-2.3**	**-2.2**	base	porous peloidal
		96-3	-13.5	-10.0	30cm above the base	microsparite and microbial
		96-4	-25.9	-10.5	70cm above the base	sparite and microbial, ghosts of gypsum crystals
		96-6A	-19.6	-10.8	130cm above the base	brecciated sparite and microbial
		96-6B	-31.1	-7.2		brecciated sparite and microbial
	III – N48°26.798’, E26°32.489’	A62/1	-39.1	-7.9	10cm above gypsum	sparite with relict microbial lamination and calcite pseudomorphs after gypsum crystals
		A62/2	-31.5	-10.9		sparite with relict microbial lamination and calcite pseudomorphs after gypsum crystals
		A62/3	-39.8	-8.9		sparite with relict microbial lamination and calcite pseudomorphs after gypsum crystals
		A64	-38.2	-7.2	70cm above gypsum	sparite with relict microbial lamination and calcite pseudomorphs after gypsum crystals
		A65/1	-32.2	-7.2	105cm above gypsum	micrite with peloidal and sparite portions and calcite pseudomorphs after gypsum crystals
		A65/2	-33.4	-8.9	105cm above gypsum	micrite with peloidal and sparite portions and calcite pseudomorphs after gypsum crystals
		A68	-3.6	-0.4	145cm above gypsum	peloidal micrite with sparite portions and veins, calcite pseudomorphs after gypsum crystals
	IV – N48°28.287’, E26°31.883’	A83	-5.7	-4.0	pocket in gypsum filled by fine-grained sandstone and limestone	bedded peloidal rock with sparite portions and relict microbial lamination
	V - N48°28.195’, E26°32.005’	A70	**-7.4**	**-3.7**	irregular limestone bed a few cm thick within gypsum	peloidal limestone with intraclasts. bioclasts (bivalves, gastropods, crinoids, echinoids, rhodoids, forams), quartz, calcite pseudomorphs after gypsum crystals
		A72a	**-10.6**	**-4.1**	irregular limestone bed a few cm thick within gypsum	peloidal-bioclastic packstone with intraclasts

TABLE I | Continued

Locality	Outcrop number (and GPS data)	Sample number	$\delta^{13}C$ [‰]	$\delta^{18}O$ [‰]	Sample location	Description of limestone
		A72b	**-8.7**	**-2.7**	irregular limestone bed a few cm thick within gypsum	peloidal-bioclastic packstone with intraclasts
		A74	**-8.8**	**-4.1**	irregular limestone bed a few cm thick within gypsum	bedded peloid rock with bioclasts (forams, echinoids, crinoids) and gypsum clasts?
		A78	**-5.0**	**-2.0**	irregular limestone bed a few cm thick within gypsum	peloid rock with abundant gypsum detritus
Anadoly	; VI – (N48°28.233', E26°31.880'	96-16	**-4.2**	**-2.5**		ooid-peloid-intraclast-quartz (also as ooid nuclei)
		96-17	**-5.6**	**-3.2**		ooid-peloid-intraclast-quartz-bioclast
		96-18	**-5.8**	**-3.3**		porous peloidal
		96-19	**-6.4**	**-5.2**		intraclast-peloidal-quartz grainstone
		96-20	**-3.8**	**-3.8**		ooidal grainstone (some ooid nuclei are quartz grains) with intraclasts and microbial portions
		A48	**-4.7**	**-4.5**	irregular bed of limestone within gypsum	porous peloidal packstone with microbial lamination
		116	**-4.2**	**-3.6**		peloid-ooid-intraclast grainstone
		117	**-0.9**	**0.5**		siltstone-mudstone rock with peloidal laminae
	VII – N48°28.464', E26°31.195'	A95/1	-18.1	-9.5	0-25cm; basal bed	peloidal packstone with ostracods and sparitic portions and pores
		A95/2	-19.5	-10.8	0-25cm; basal bed	sparite with relics of peloidal packstone
		A97	-26.6	-10.1	42cm above the base	sparite with relict microbial lamination
		A99	-21.4	-11.1	75cm above the base	sparite with relict microbial lamination and calcite pseudomorphs after gypsum crystals
		A52	-16.4	-9.4	109cm above the base	micrite with sparitic portions (including pore fillings) and relict microbial lamination
		A53	-22.3	-12.2	135cm above the base	micrite. microsparite and sparite, with relics of microbial lamination
		A55/1	-16.3	-4.7	215cm above the base	brecciated peloidal rock, with calcite pseudomorphs after gypsum crystals
		A55/2	-17.6	-5.5	215cm above the base	brecciated peloidal rock, with calcite pseudomorphs after gypsum crystals
		A94	-10.3	-4.3	240cm above the base	microbial with laminae of peloidal packstone, quartz, calcite pseudomorphs after gypsum crystals
		A92	-11.4	-4.0	275cm above the base	peloidal packstone
Lozyna	I	96-1	**-9.0**	**-5.4**	30cm above the base; laminated	fine-grained peloidal-intraclast grainstone
		96-2	-12.6	-6.4	5cm above the base	peloidal-intraclastic grainstone with strongly recrystallised portions
		96-3	**-6.2**	**-4.5**	5cm above the base	peloidal-intraclastic grainstone (fine quartz, glaucony), local cellular texture
		96-5A	-21.3	-9.8	10cm above the base	microsparite with sparitic dedolomite parts and sparitic veins
		96-5B	-24.2	-9.8		microsparite with sparitic dedolomite parts and sparitic veins
		96-7A	-22.0	-9.3	110cm above the base	microsparite with sparitic veins and portions
		96-7B	-21.0	-9.5		microsparite with sparitic veins and portions
		96-9	**-19.9**	**-9.8**	240cm above the base; massive	finely porous mudstone with quartz

TABLE I | Continued

Locality	Outcrop number (and GPS data)	Sample number	$\delta^{13}C$ [‰]	$\delta^{18}O$ [‰]	Sample location	Description of limestone
Lozyna	I	96-10A	-17.8	-9.0	150cm above the base	sparite with local laminated mudstone and microbial portions
		96-13A	-21.3	-8.7	340cm above the base; the	porous sparite and microsparite with microbial relics
		96-13B	-22.3	-8.8	uppermost part	porous sparite and microsparite with microbial relics
	III	98-2	**-4.5**	**-3.0**	1.5m above the base (brown limestone)	peloidal-intraclast packstone with quartz
		98-3	**-18.0**	**-8.4**	1.5m above the base	mudstone rock with peloids
		98-5	**-18.1**	**-8.3**	6.0m above the base	peloidal-microbial
		98-6.1	**-9.9**	**-4.6**	6.5m above the base (hard	peloidal-intraclast packstone
		98-6.2	**-4.4**	**-3.5**	limestone)	peloidal-intraclast packstone
		98-7	**-11.1**	**-6.7**	7.0m above the base	peloidal-intraclast packstone
Pyshchatyntsi		1	-18.2	-10.5	1.5m above the base	recrystallised peloidal-microbial – veins and portions of sparite, calcite pseudomorphs after gypsum crystals
		2	**-10.4**	**-3.7**	5.0m above the base	peloidal packstone
		3	-11.0	-4.5	6.0m above the base	peloidal packstone-grainstone with portions of very fine calcite pseudomorphs after gypsum crystals
		4	**-1.3**	**0.9**	contact with the Ervilia Bed	porous bedded peloidal packstone-grainstone with relict microbial lamination
		5.1	-15.5	-11.3	20cm above the base	microsparite with sparite veins and portions and peloidal portions, calcite pseudomorphs after gypsum crystals
		5.2	-15.4	-10.7		microsparite with sparite veins and portions and peloidal portions, calcite pseudomorphs after gypsum crystals
		6	-16.5	-11.2	above the sample B	microsparite with sparitic veins and portions and peloidal portions
		B	**-7.8**	**-3.2**	above the Ervilia Bed	peloidal wackestone
		C	-13.3	-8.6	100cm above the base	recrystallized bedded microbial with peloidal portions and calcite pseudomorphs after gypsum crystals
		D	-8.5	-3.7	200cm above the base	brecciated sparite with peloid portions and calcite pseudomorphs after gypsum crystals
		E	**-4.5**	**-4.4**	450cm above the base	bedded peloid-intraclast packstone-grainstone
		1998/2.2	**-17.6**	**-11.3**	base	peloidal wackestone with relict microbial lamination
Hlybochok		33A	-16.0	-11.8	base of section	sparite with rare microbial
		33B	-16.7	-11.3		sparite with rare microbial and calcite pseudomorphs after gypsum crystals