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Strontium isotope composition of Badenian (Middle Miocene) Ca-sulphate deposits in West Ukraine: a preliminary study

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Strontium isotope compositions have been measured in six primary gypsum samples from the most marginal part of the Badenian evaporite succession in the Ukrainian Carpathian Foredeep Basin (Mamalyha quarry section) and in two anhydrite samples from the basin-centre halite zone of the Ukrainian Carpathian Foredeep, aimed determining the origin of brines from which these sulphates were precipitated. The strontium isotope ratios (^{87}Sr/^{86}Sr) of halite facies-associated anhydrite samples are very similar (0.708902 and 0.708917, respectively) and higher than the ratio infferred for Badenian seawater. The strontium isotope ratios (^{87}Sr/^{86}Sr) of six samples of primary gypsum from Mamalyha range from 0.709154 to 0.709838; thus they are strongly divergent from coeval oceanic values. The gypsum from the lower part of the Mamalyha section shows much higher ^{87}Sr/^{86}Sr ratios than the gypsum from the upper part and a clear decreasing-upwards trend is observed. The higher strontium isotope ratios are related to the portion of the gypsum section showing both δ^{18}O and δ^{34}S divergent from coeval oceanic values. The ^{87}Sr/^{86}Sr ratios of minerals in marine, bedded evaporite deposits are commonly higher than that of contemporaneous seawater which is often explained in terms of secondary origin or recrystallization of these minerals in the presence of radiogenic ^{87}Sr-bearing fluids, mostly from a detrital source, but the Mamalyha primary gypsum is very pure and clay intercalations are very thin and rare. High radiogenic ^{87}Sr/^{86}Sr ratios in primary gypsum of the Mamalyha quarry indicate an important radiogenic strontium non-marine contribution to the Badenian basin.

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Key words: Middle Miocene, evaporites, strontium isotopes, gypsum, Paratethys.

INTRODUCTION

Many ancient evaporite deposits interpreted as marine in origin in fact have a more complex origin. A study based on X-ray microanalysis of primary fluid inclusions in halite, isotopic analysis (δ^{34}S and δ^{18}O in sulphates), and computer-based evaporation models, suggested recharge proportions during Badenian halite precipitation of the Polish Carpathian Foredeep of between 20–30% seawater and 65–70% continental water, with 5–10% of the continental waters recycling previously precipitated halite (Cendón *et al.*, 2004). As the restriction was smaller during the sulphate precipitation and thus recharge proportion was in favour of seawater, the Badenian sulphate evaporites could have precipitated from water dominated by an oceanic source (Flecker and Ellam, 2006). This in turn encourages to apply strontium isotope stratigraphy (McArthur *et al.*, 2001) as the Sr isotopic composition of Miocene seawater is very well-established (e.g., Hodell *et al.*, 1991; McArthur *et al.*, 2001).

Kasprzyk *et al.* (2007) reported ^{87}Sr/^{86}Sr ratios from 0.708915 to 0.716329 in six samples of Badenian sulphates from Poland. They found that sedimentary gypsum displays strontium isotope ratios close to contemporaneous (Badenian) seawater and anhydrite samples have more radiogenic ^{87}Sr/^{86}Sr ratios than the gypsum samples. The high ^{87}Sr/^{86}Sr ratios in anhydrite samples were interpreted as resulting from the mixing of fluids of two different isotopic signatures, i.e., marine waters and continental waters, during sulphate deposition and diagenesis, and gypsum was regarded as having formed from marine brines that were subject to an important inflow of continental waters (Kasprzyk *et al.*, 2007).

The samples studied by Kasprzyk *et al.* (2007) derived from the sulphate basin and the adjacent gypsum Zone III of Peryt (2006). In this paper we present results of the study of coeval Ca-sulphates of the Tyras Formation (Fig. 1) from the Mamalyha

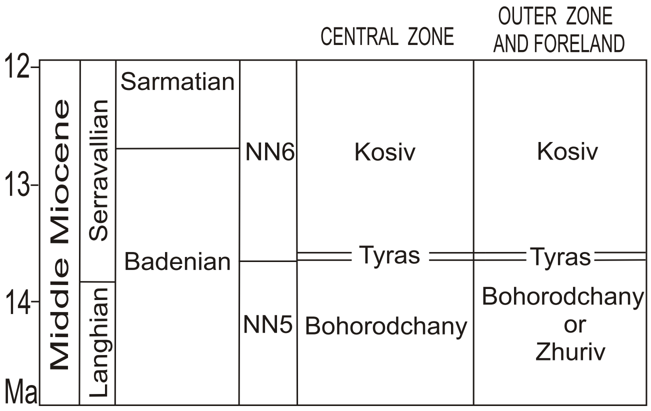

Fig. 1. Stratigraphic location of the Tyras Formation and adjacent strata in the central zone of the Ukrainian Carpathian Foredeep and its outer zone and foreland (after Oszczypko *et al*., 2006, supplemented)

The Miocene time scale after Hilgen *et al*. (2009), partly recalibrated and correlated to regional stages of the Central Paratethys. The Badenian–Sarmatian boundary after Harzhauser and Piller (2004). Calcareous nannoplankton zones *sensu* Peryt (1997). The lower limit of Badenian evaporites after de Leeuw *et al*. (2010) and the upper limit after Bukowski *et al*. (2010)

section located in the most marginal facies zone (Zone I of Peryt, 2001) as well as from the halite basin zone in West Ukraine (Fig. 2) what allows a more comprehensive understanding of controls on the strontium isotope composition of Badenian sulphates. The Mamalyha section was chosen because it was earlier subject both to the study of minor and trace elements including strontium content (Ryka, 1994), and to the study of sulphur and oxygen isotopes (Peryt, 2001) that are helpful in examining the origin of sulphates, particularly when combined with the use of strontium isotopes (Lu and Meyers, 2003).

GEOLOGICAL SETTING

The Ukrainian Carpathian Foredeep Basin formed northeast of the overthrusting Carpathian nappes (Oszczypko *et al*., 2006). The Badenian evaporites occur in the outer (Bilche–Volytsya) tectonic zone and the foreland as well as in the central (Sambir) tectonic zone (Vul *et al*., 1998; Figs. 1 and 2). In the outer zone, Badenian evaporites are included into the Tyras Formation (Petryczenko *et al*., 1994; Andreyeva-Grigorovich *et al*., 1997) which consists of Ca-sulphates (usually 10–20 m thick) with claystone intercalations in the basinal facies. Petrographic study of Badenian anhydrites of the basinal facies in the Carpathian Foredeep of Eastern Poland and West Ukraine showed that they display extensive pseudomorphic features inherited from the precursor gypsum, and that anhydritization was a diachronous process that started in the basin centre under sedimentary conditions; the successive phases of anhydrite formation occurred along with subsidence undergone by the foredeep basin (Kasprzyk and Ortí, 1998). In local depressions Ca-sulphates occur with rock salt and claystone intercalations of considerably greater thickness (up to 275 m, Panow and Płotnikow, 1996); in the Kalush area in borehole No. 12 the thickness of the rock salt with anhydrite is 118 m (Panow and Płotnikow, 1996).

The stratigraphic position of evaporites occurring within the Sambir tectonic zone, and particularly of potash deposits in the Kalush area, is subject to discussion (Hryniv *et al*., 2007, with references therein) but there also occurs the Tyras Formation that attains 40 m in thickness and is composed of massive anhydrite followed by anhydrite interbedded with clayey and sandy-clayey beds (Korenevskiy *et al*., 1977) and intercalation(s) of rock salt (Kuźniar, 1935; Panow and Płotnikow, 1996). In the Hrynivka 525 borehole located south of Kalush (Fig. 2), evaporites occur in the depth interval of 280–541 m and they usually show a dip of 30°. The borehole did not drill through the entire evaporite sequence consisting of rock salt with intercalations (1–5.5 m thick) of salt breccia, anhydrite and clay (Fig. 3). The content of halite varies from 70.7 to 94.2% (the average is 76.3%), and the average contents of anhydrite and water-insoluble residue content are 11.9% and 11.8%, respectively (Stupnitskiy *et al*., 1978). The mean bromine content in halite is 36 ±15 ppm (Galamay *et al*., 2009). Halite is usually dark grey in colour; in places, especially when anhydrite nodules co-occur, it is bedded. In the Hrynivka 522 borehole which is located 475 m SW of the Hrynivka 525 borehole, the rock salt is only 10 m thick (Stupnitskiy *et al*., 1978; Khrushchov, 1980, p. 258), and it is cut by overthrusted Balych deposits. In the Hrynivka 528 borehole, located 4 km south of the Hrynivka 525 borehole, the thickness of rock salt is 65.5 m (Stupnitskiy *et al*., 1978).

In the Selets'-Stupnytsya area (located 12 km SE of Sambir) the evaporites (60–250 m thick) are underlain by siliciclastic deposits of the Bohorodchany Formation and are overlain by the Kosiv Formation (mostly clays). Microfaunal data indicate a Badenian age for the evaporites and the adjacent strata (Venglinskiy and Kopystyanskaya, 1979; M. A. Klimov in Khrushchov, 1980, p. 258). Klimov (1974) considered that evaporites belong to the Tyras Formation and Korenevskiy *et al*. (1977, p. 60, fig. 25) concluded that they are of Karpatian age and correlated them with the Kalush beds (applying present stratigraphical terms). In the borehole Selets'-Stupnytsya 348, the rock salt succession occurs in the depth interval of 117.4–176.1 m (Fig. 4); it is folded and the dips range from 10 to 50° (Petrichenko *et al*., 1974). It comprises, in addition to halite (the content of which varies from 63 to 99.5% in various parts of the succession), also anhydrite, clay and salt breccia interbeds (up to *ca*. 5 m thick) and one polyhalite bed (0.3 m thick; Petrichenko *et al*., 1974). The mean bromine content in halite is 79 ±29 ppm (Kovalevich, 1976). The rock salt unit underlain by siliciclastic deposits (claystones, sandstones and siltstones) with thin laminae of satin-spar gypsum and halite; in addition, at the depth of 211.5–212.0 finely crystalline anhydrite occurs. The siliciclastic deposits included into the Tyras Formation are underlain by siltstones of the Bohorodchany Formation (Klimov and Korzun, 1975); the boundary is put at the depth of 236.0 m (Fig. 4).

In the Carpathian foreland, the Tyras Formation consists of gypsum and the Ratyn Limestone. The gypsum is several tens of metres thick and forms a wide (up to 100 km) marginal Ca-sulphate platform. In its most marginal part (>15 km wide, the gypsum facies zone I), the gypsum section consists entirely of stromatolitic gypsum which exhibits a considerable variety of forms, although planar or slightly crenulated stromatolites

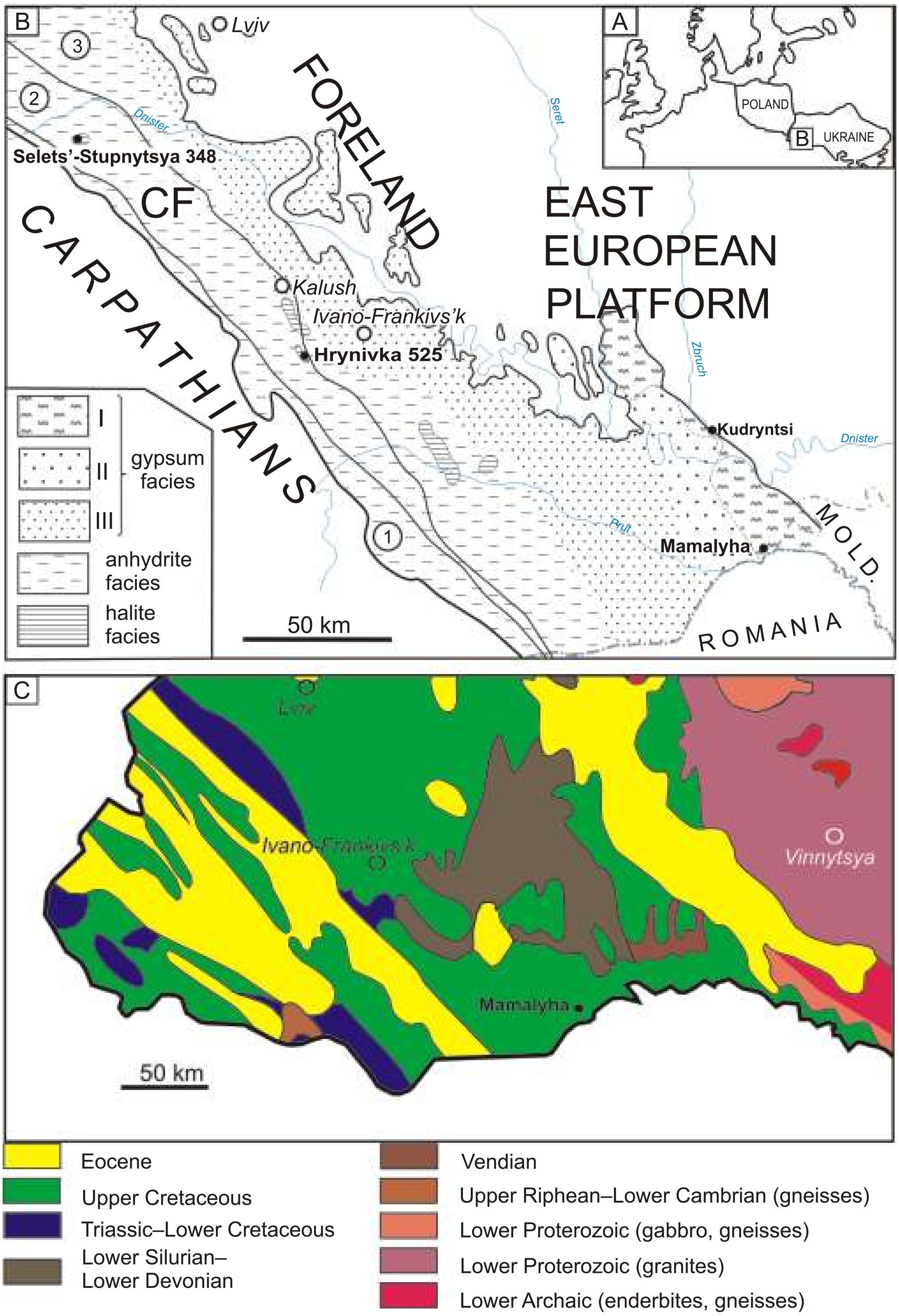

Fig. 2A – location of area studied; B – map showing the location of the boreholes studied (Selets'-Stupnytsya 348 and Hrynivka 525) and the Mamalyha outcrop tectonic zones of the Carpathian Foredeep (CF) after Vul *et al.* (1998): 1 – Boryslav–Pokuttya Zone; 2 – Sambir Zone; 3 – Bilche–Volytsya Zone; facies zones of Badenian sulphates after Peryt (2006); in the Sambir Zone only halite facies zones discussed in the text are shown; C – geological map of area studied without deposits younger than Paleogene (after Halets'kyy, 2001)

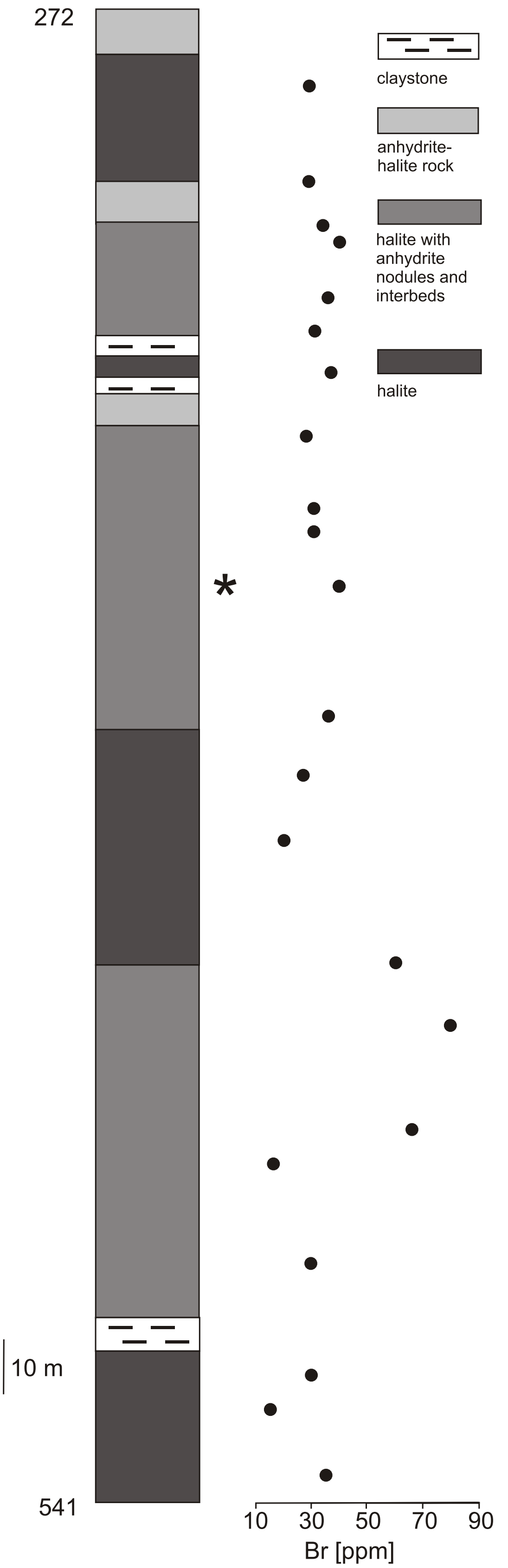

Fig. 3. Section of the Hrynivka 525 borehole (after Stupnitskiy *et al.*, 1978)

Bromine data after Galamay *et al.* (2009); asterisk shows the location of the sample studied; depth in metres

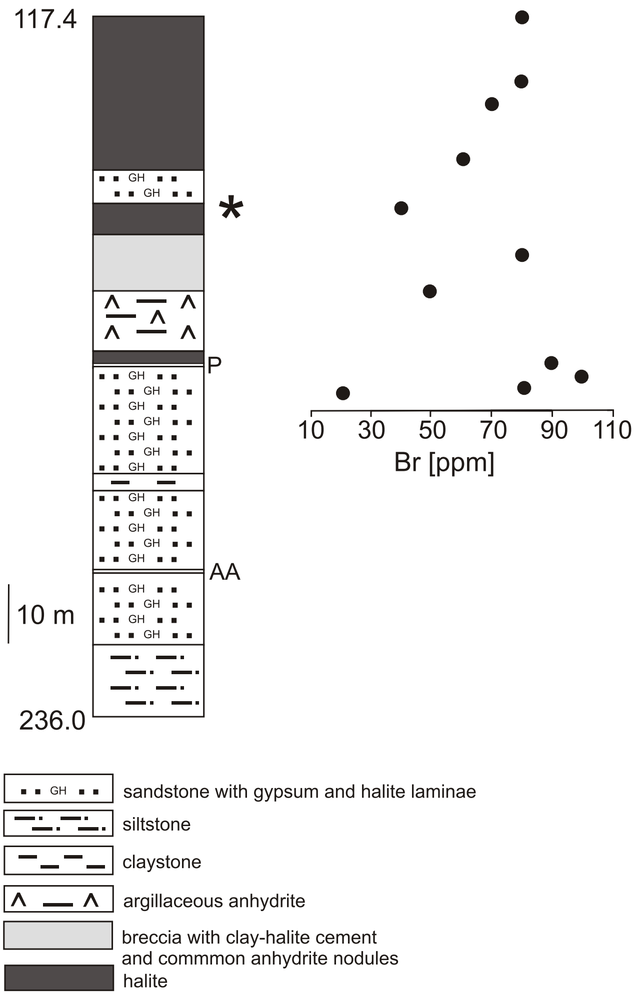

Fig. 4. Section of the Selets'-Stupnytsya 348 borehole (after Klimov and Korzun, 1975)

Bromine data after Kovalevich (1976); asterisk shows the location of the sample studied; P – polyhalite bed; AA – thin bed of argillaceous anhydrite; depth in metres

prevail (Figs. 5–8; Peryt, 1996, figs. 12 and 13; 2001). The gypsum facies zone II (> 40 km wide) is located basinward of the facies zone I and is characterized by the occurrence of stromatolitic gypsum in the lower part of the section and sabre gypsum in the upper part (Peryt, 2001). In facies zone I and the adjacent part of facies zone II there is a clear channelized surface in the upper part of the stromatolitic gypsum sequence covered by lenticular limestones (up to 20 cm thick in the Kudryntsi section) showing mudstone and wackestone textures and bioclasts indicating their marine provenance (Peryt, 2001; Peryt and Peryt, 2009). A similar surface, showing a relief of several centimetres, was recorded 8.3 m below the Ratyn Limestone in Mamalyha (Figs. 5 and 8A; Peryt, 2001, fig. 14), and the depressions are filled with bioclastic and peloidal limestone (Peryt, 2001). There are other horizontal discontinuity surfaces that usually can be traced throughout the entire Mamalyha quarry (Peryt, 2001; Bąbel *et al.*, 2009). Most of them are covered by clayey and marly material, and in some thicker marly intercalations in the lower part of the gypsum sections current ripples occur, as recorded by Bąbel *et al.* (2009). In one interca-

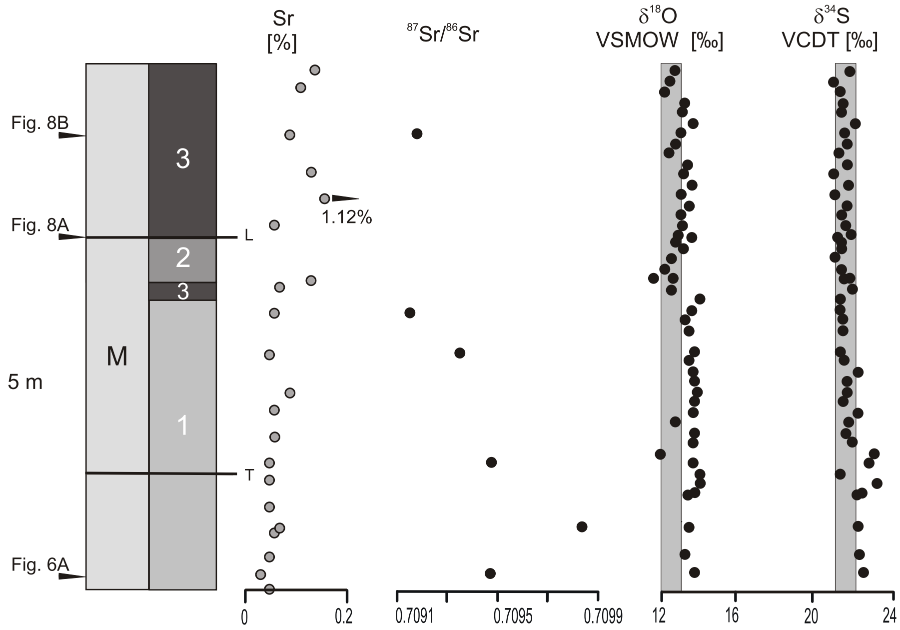

Fig. 5. Mamalyha quarry section, showing macroscopic aspects (left column) and microscopic aspects (right column)

M – microbialitic gypsum; 1 – well-developed microbialitic gypsum; 2 – poorly developed microbialitic gypsum with thin selenite laminae; 3 – stromatolitic laminae with syngenetic celestite occurrences; the Sr content, ^{87}Sr/^{86}Sr ratios, and δ^{34}S and δ^{18}O values (after Peryt, 2001). Contemporaneous seawater δ^{34}S and δ^{18}O values (grey fields) after Paytan *et al.* (1998) and Zak *et al.* (1980); T – intercalation with pyroclastic material (see Bąbel, 2005*a*; Bąbel *et al.*, 2009; Fig. 8); L – lenticular limestone intercalation (see Peryt, 2001, fig. 14)

lation (T in Fig. 5) pyroclastic material is reported (Bąbel 2005*a*; Bąbel *et al.*, 2009; Fig. 8B).

Penetrations of the calcareous material from the overlying Badenian strata are common in the Mamalyha quarry. The Badenian karstification was related to subaerial exposure of the gypsum strata during or soon after gypsum deposition (Peryt *et al.*, 1998). The limestone filling the supposed karst cavities is mostly peloidal packstone with bioclasts (foraminifers, shells) and gypsum clasts. Stable isotope values obtained from the limestone infills were –2.6 to –6.2‰ δ^{18}O and –0.8 to –2.8‰ δ^{13}C (n = 4), thus similar to those found in the Ratyn Limestone of Criva (Peryt and Peryt, 1994). The gypsum in the Mamalyha quarry rests on lower Badenian sands and marls (3–4 m thick), which in turn overlie eroded Cretaceous siliceous limestones (*ca*. 10 m thick; Klimchouk and Andrejchuk, 2005). The upper Badenian gypsum sequence is *ca*. 25 m thick and consists of stromatolitic gypsum with common intercalations of clastic, laminated gypsum (Peryt, 1996) and locally occurring selenite-microbialite gypsum (Bąbel, 2005*b*; Fig. 5). Petrographic study of inferred microbialitic gypsum showed that they consist of interlaminated gypsum (showing various crystal sizes) and micritic carbonate (possibly calcite); the thickness of carbonate laminae is usually 0.1–0.3 mm, and gypsum laminae are usually thicker (up to 2 mm). In general, the carbonate is sparse com-

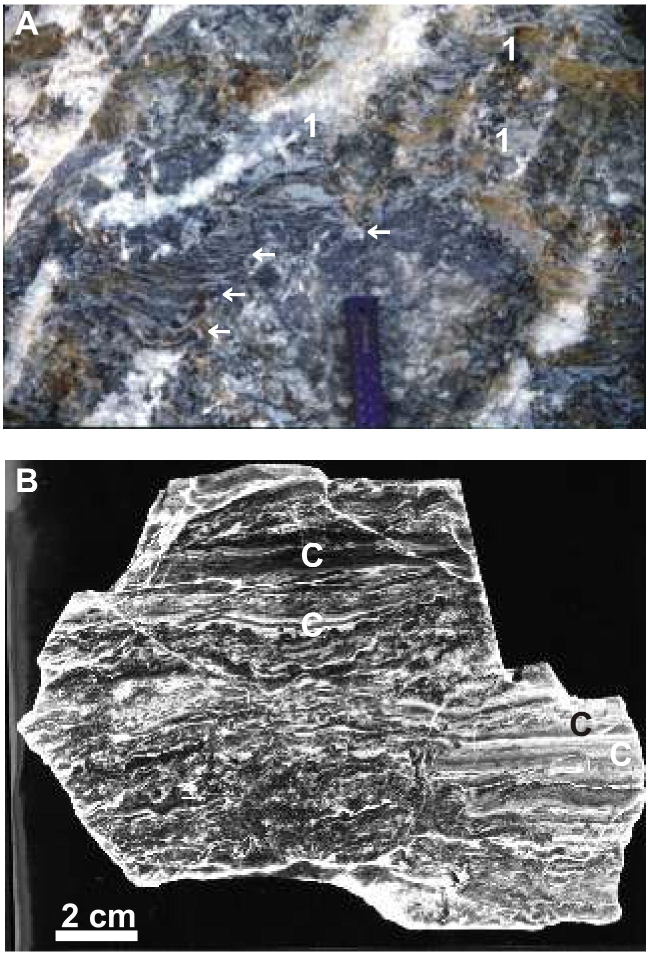

Fig. 6. A – gypsum from the lowest part of the Mamalyha section (0–3 m above the base) showing very common limestone veins and encrustations (1) and channel (arrowed) fillings; B – stromatolitic gypsum with common intercalations of clastic gypsum (C) (loose sample)

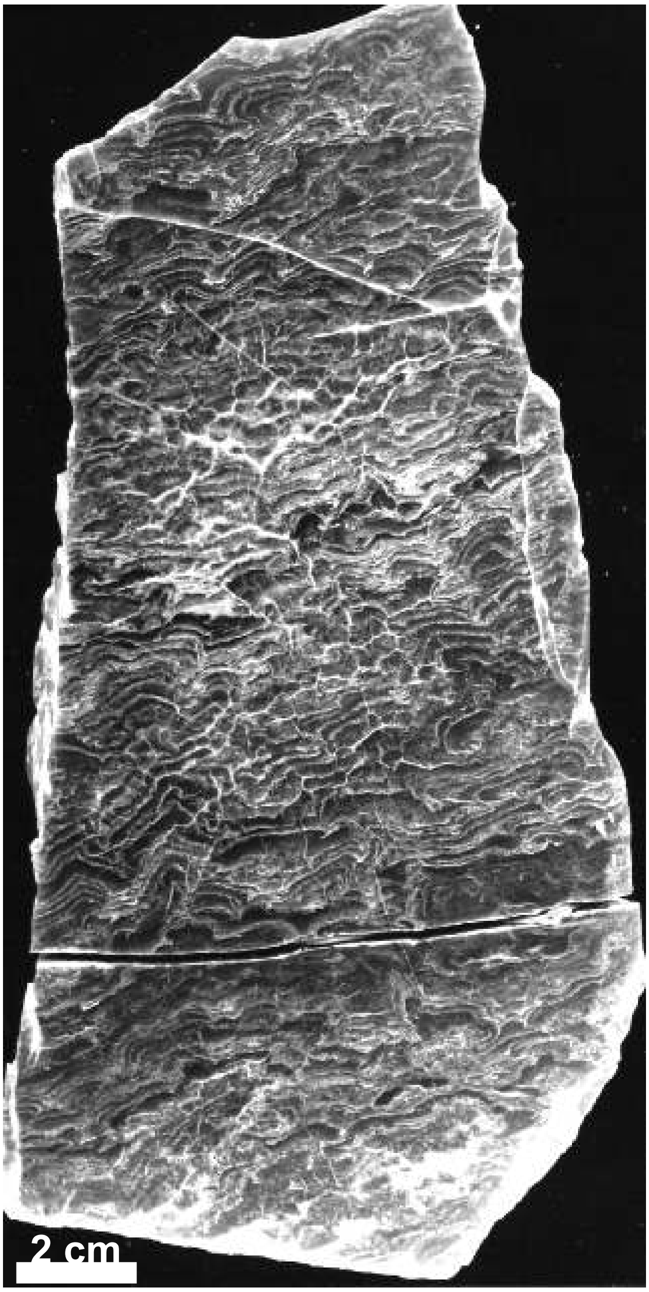

Fig. 7. Stromatolitic gypsum (Mamalyha, loose sample) showing common crenulations

pared to Badenian stromatolitic gypsum described by Kasprzyk (1993), yet in some thin sections ghosts of vertically-oriented algal filaments (1–3 mm long and 0.02–0.2 mm thick) can be seen. In the upper part of gypsum section discontinuous, short (3–10 mm long) laminae of upright-growth small (1–3 mm) gypsum crystals characterized by sharp ends are quite common. The terminations of larger crystals are locally cut, which indicates erosion and/or corrosion (*cf.* Kasprzyk, 1993).

The gypsum of the Mamalyha quarry is primary (Peryt, 1996, 2001) and thus the original gypsum microbialitic deposits preserve sedimentary fabrics. Gypsum cementation occurred under the influence of sedimentary brines. Rarely, epigenetic celestite occurs that has precipitated in lithified deposit from diagenetic fluids that were enriched in strontium; the celestite occurrence is related to voids formed after dissolved carbonate cements or to boundaries of gypsum crystals.

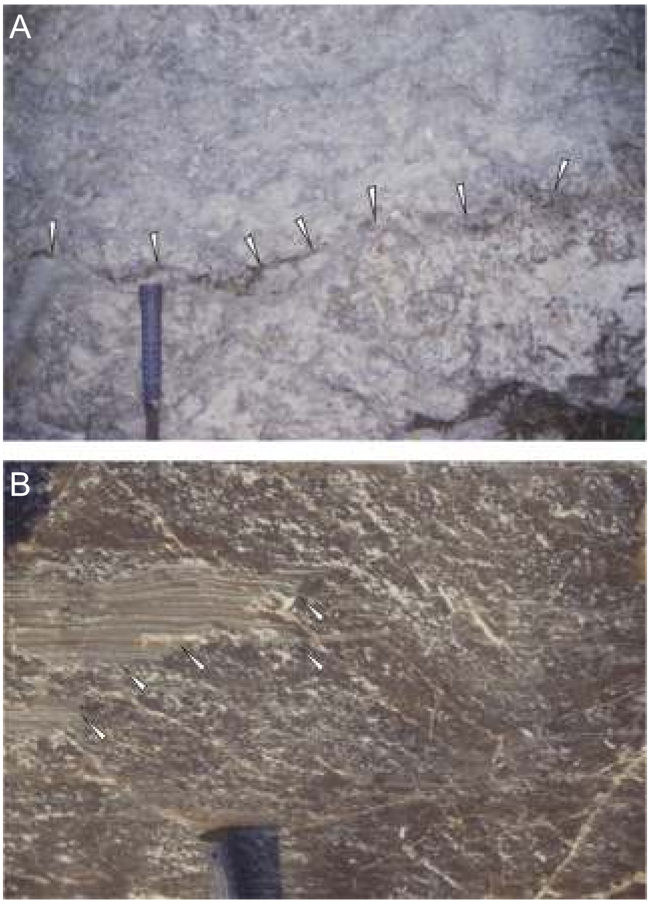

Fig. 8. A – the location of the distinct boundary within the upper portion of the Mamalyha gypsum section (arrowed; see Fig. 5 and Peryt, 2001, fig. 14) that in places is covered by lenticular limestone. The brecciated appearance of gypsum below the boundary is a weathering feature (Peryt, 2001); B – channel (arrowed) filled by clastic gypsum within the stromatolitic gypsum from the upper part of the Mamalyha gypsum section

The top of gypsum is karstified and covered by the Ratyn Limestone (Peryt and Peryt, 1994) followed by rhodoid limestones and marls.

MATERIAL AND METHODS

Eight samples have been taken from the upper Badenian Tyras Formation: two from anhydrites (one from the Hrynivka 525 borehole and one from the Selets'-Stupnytsya 348 borehole) and six from gypsum of the Mamalyha quarry (Figs. 2–5). In the case of the Mamalyha section, two samples previously analysed for sulphur and oxygen isotopic composition (Peryt, 2001) were selected, and four others come from another sample set of gypsum from West Ukraine (including 21 samples from Mamalyha) in which major, minor and many trace elements were determined with the use of ICP in accredited laboratories of the Polish Geological Institute and summarized by Ryka (1994). The samples studied are characterized in Table 1.

Table 1

Sample description and results

SPH collection number	Sample description	Sr content [%]	^{87}Sr/^{86}Sr	^{87}Sr/^{86}Sr normalized to 0.710248 SRM987 value	Sample location	δ^{34}S [‰] and δ^{18}O [‰] (after Peryt, 2001)
Hrynivka 525 borehole						
1354	Small (2–10 mm) anhydrite nodules arranged in discontinuous laminae in rock salt composed of elongated (2–4 mm) halite crystals and bigger (10–15 mm) porphyroid rounded halite grains	no data	0.708917 ±9	0.708902	depth 376 m	no data
Selets'-Stupnytsya 348 borehole						
904	Nodules (5–20 mm) of blue anhydrite from clayey rock salt (halite content: 63%)	no data	0.708932 ±11	0.708917	depth 149 m	no data
Mamalyha quarry						
MAM 38	Microbialitic gypsum: alternated diffuse gypsum laminae (1–2 mm thick) made of crystals of various sizes (0.05–0.1 and 0.1–0.3 mm) and diffuse thin laminae of microcrystalline carbonate	0.03	0.709486 ±15	0.709471	0.7 m above the base of gypsum	22.7 and 13.9
MAM 36	Microbialitic gypsum: alternated subparallel gypsum laminae made of crystals of various sizes (<0.01–0.04 and 0.04–0.1 mm) and carbonate laminae; laminae are 0.1 to 2 mm thick	0.07	0.709853 ±9	0.709838	3.0 m above the base of gypsum	22.4 and 13.6
MAM 32	Microbialitic gypsum: alternated thin (0.3–2 mm) not parallel gypsum laminae made of gypsum crystals of various sizes (<0.01–0.04 and 0.04–0.1 mm) and diffuse very thin (<0.1 mm) laminae of microcrystalline carbonate	0.05	0.709494 ±12	0.709479	6.2 m above the base of gypsum	23.0 and 13.8 (adjacent sample)
MAM 27	Microbialitic gypsum: alternated thin (0.5–3 mm) gypsum laminae made of gypsum crystals of various sizes (<0.01–0.02 and 0.04–0.1 mm) and rare very crenulated, thin (0.1–0.2 mm, rarely up to 1 mm) laminae of microcrystalline carbonate. In addition, thin (0.1–0.2 mm) laminae of vertically-arranged parallel gypsum crystals occur	0.05	0.709372 ±8	0.709357	11.5 m above the base of gypsum	21.5 and 13.9 (adjacent sample)
MAM 26	Microbialitic gypsum: alternated thin (0.5–2 mm) gypsum laminae made of gypsum crystals of various sizes (0.01–0.02; 0.1–0.4; and 0.3–0.4 mm) and carbonate laminae (1–2 mm thick)	0.06	0.709169 ±11	0.709154	13.5 m above the base of gypsum	22.2 and 12.7 (adjacent sample)
MAM 13	Elongated gypsum crystals (0.5–3 mm) with sharp tops, oriented in various directions, arranged in patches and diffuse laminae occurring within the mass of fine (0.02–1 mm) equidimensional gypsum crystals with dispersed carbonate material. In addition, rare thin discontinuous carbonate laminae and vertically-arranged selenite crystals (1 mm long) occur	0.09	0.709195 ±17	0.709180	22.3 m above the base of gypsum and 3.2 m below the Ratyn Limestone	21.8–22.3 and 13.2–13.8 (adjacent samples)

The strontium isotope compositions were analysed at the Isotope Geochemistry Laboratory, Kraków Research Centre of the Institute of Geological Sciences, Polish Academy of Sciences. 50–100 mg of powdered rock sample was dissolved on a hot plate in 2.5 to 6N HCl. 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. After converting to nitrates, the sample was analysed by MC ICPMS Neptune in 2% HNO_3. Analyses were carried out in a static mode and performance of the instrument was monitored by frequent analyses of SRM987 standard. Isotopic ratios were corrected for instrumental mass bias by normalizing to ^{86}Sr/^{88}Sr = 0.1194 using exponential law. Reproducibility of the SRM987 over the period of analyses was ^{87}Sr/^{86}Sr = 0.710263 ±13 (measurement precision error, n = 4), which is identical with long term reproducibility for nearly 2 years period ^{87}Sr/^{86}Sr = 0.710263 ±13 (measurement precision error, n = 180). The obtained results were normalized to recommended SRM987 value ^{87}Sr/^{86}Sr = 0.710248. Precision of individual ^{87}Sr/^{86}Sr ratios in Table 1 refers to the last significant digits and is at 2SE level. Total procedure blank was below 50 pg.

The ^{87}Sr/^{86}Sr record can be used for various purposes, including dating and correlation of marine sediments and estimation of the duration of stratigraphic gaps, biozones and stages (McArthur *et al.*, 2001, with references therein). Howarth and McArthur (1997) compiled ^{87}Sr/^{86}Sr data and fitted to them a nonparametric LOWESS statistical regression function, and thus it is possible to convert quickly and easily from ^{87}Sr/^{86}Sr to numerical age. We have applied their LOWESS Version 4: 08/04 (McArthur *et al.*, 2001) to estimate the ^{87}Sr/^{86}Sr ratio of the Badenian seawater from numerical age.

RESULTS

The strontium isotope composition of the samples studied is shown in Table 1.

The strontium isotope ratios ($^{87}Sr/^{86}Sr$) of two anhydrite samples from Hrynivka and Selets'-Stupnytsya are very similar (0.708902 and 0.708917, respectively); they are higher than the ratio of the Badenian contemporary seawater. Assuming that the Badenian gypsum was formed some time between 13.81 and 13.5 Ma, the times being controlled by Badenian tuffite dating (Bukowski *et al.*, 2010; de Leeuw *et al.*, 2010) and the occurrence of Badenian sulphates in the lower part of the NN6 Discoaster exilis Zone (Peryt, 1997, 1999; *cf*. Raffi *et al.*, 2006), and taking into consideration the upper and lower confidence limits (McArthur *et al.*, 2001), the resulted $^{87}Sr/^{86}Sr$ values should be between 0.708800 and 0.708809.

The strontium isotope ratios ($^{87}Sr/^{86}Sr$) of the Mamalyha gypsum vary from 0.709154 to 0.709838 and are strongly divergent from coeval oceanic values. The gypsum from the lower part of the section shows much higher ratios than the gypsum from the upper part; a clear decreasing-upwards trend is observed (Table 1). The higher strontium isotope ratios are related to the portion of the gypsum section showing both $\delta^{18}O$ and $\delta^{34}S$ divergent from coeval oceanic values (Fig. 5).

The results of chemical analyses make it possible to subdivide the Mamalyha section into two parts, with the boundary between them being located *ca*. 14 m from the base of the gypsum section; at that boundary also the petrographical nature of the gypsum changes: below it microbialitic gypsum occurs, and above it thin selenitic gypsum laminae occur. At this boundary one can observe an increase in $\delta^{34}S$ values, a decrease in $\delta^{18}O$ values, and an increase in Sr, Ba and Mn contents (Fig. 5). In the lower part the contents of those minor elements are: 0.06%; 24 ppm; and 4 ppm; and in the upper part 0.11%; 64 ppm; and 22 ppm, respectively. The mean Sr content in Mamalyha is 0.07 ±0.03 (n = 20) if one relatively high value of 1.12% is omitted, thus it is lower than recorded in the set of 124 analyses from the entire Carpathian Foredeep Basin analysed by Ryka (1994) which yielded a value of 0.13%. Nevertheless, the Sr contents in Mamalyha are within the expected contents of marine-derived non-selenitic facies (Playà and Rosell, 2005) although there occur small (0.03 mm) isometric crystals of celestite or more rare prismatic celestite crystals (0.04–0.1 mm long) with rounded ends; the celestite is probably syngenetic and occurs below the limestone intercalation shown in Figure 8A. The celestite crystals in the sample showing high Sr content (1.12%; Fig. 5) are larger (0.1–0.5 mm), idiomorphic, and clearly located in spaces between gypsum crystals; they are of epigenetic origin. The mean values for Ba and Mn are 39 ±35 ppm and 11 ±15 ppm, respectively. The purity of gypsum (ignoring the siliciclastic laminae) is expressed in very low Fe and Al contents (0.01–0.06% and 0.01–0.07%, respectively). The content of many other elements is at analytical limits (Ryka, 1994).

The sulphur and oxygen isotope studies of Mamalyha gypsum (n = 48) showed that the range of $\delta^{34}S$ values is 21.2 to 23.4‰, and the mean $\delta^{34}S$ value is 21.9 ±0.5‰. The mean $\delta^{18}O$ value is 13.3 ±0.6‰, and the range is 11.8 to 14.2‰ (Peryt *et al.*, 2002). Both $\delta^{18}O$ and $\delta^{34}S$ values show a general slight decrease upwards (Fig. 5). The majority of $\delta^{18}O$ values are higher than the expected value with respect to the contemporaneous ocean water values of dissolved marine sulphate, and only in the upper part of the gypsum section are marine values common (Fig. 5). The $\delta^{34}S$ values are mostly marine except that clearly higher values occurring in the lowermost part of the section (Fig. 5).

INTERPRETATION AND DISCUSSION

The strontium isotope ratios of anhydrite samples from Hrynivka and Selets'-Stupnytsya are slightly increased compared to the contemporaneous ocean water values, and the Mamalyha gypsum section shows very radiogenic $^{87}Sr/^{86}Sr$ compared to the ratios expected for a Middle Miocene open ocean (Hodell *et al*., 1991; McArthur *et al*., 2001). The Sr isotope compositions of evaporites reflect (1) the composition of the mother brines and/or (2) interactions between the brines and rocks within the evaporite basin (e.g., Lu and Meyers, 2003; Palmer *et al*., 2004). Sr isotope ratios divergent from coeval oceanic water values indicate that the proportion of oceanic water entering the basin was less than *ca*. 50% and that brines derived mostly from river run-off and rain water (Flecker and Ellam, 2006). The riverine runoff was from two main directions. The first was the East European Platform and the second was the Carpathian area. There are no available Sr isotope data for non-marine fluids (river water or groundwater) in the study area. The bulk of the Carpathians is built of Mesozoic and Paleogene rocks and one would expect a dominant influence of Sr from those rocks, i.e. the Sr-isotope ratios should be lower than those for contemporary Miocene seawater (see e.g., Kocsis *et al.*, 2009), and not higher. Similarly, the rocks exposed on the East European Platform during Badenian gypsum deposition were mostly earlier Badenian, Cretaceous or Vendian–Silurian in age, and only some 100 km to the east lower Proterozoic and lower Archaic crystalline rocks, mostly gneisses, occur (Fig. 2C). Very old rocks, especially those rich in potassium, have high $^{87}Sr/^{86}Sr$ ratios: the mean strontium isotopic ratio in major world rivers is 0.7119 (Palmer and Edmond, 1992) which is high relative to modern seawater (0.7092), but there are reported values of $^{87}Sr/^{86}Sr$ as high as 0.73844 from streams draining old (>1000 Ma) igneous and metamorphic rocks in Canada (Wadleigh *et al*., 1985). During weathering of those rocks, the $^{87}Sr/^{86}Sr$ remained either unmodified or increased only slightly in the weathered residue (Dasch, 1969), but differences in the distribution of radiogenic and non-radiogenic strontium in the main minerals in the soil mean that the $^{87}Sr/^{86}Sr$ ratios of the bulk soils are different to the ratios

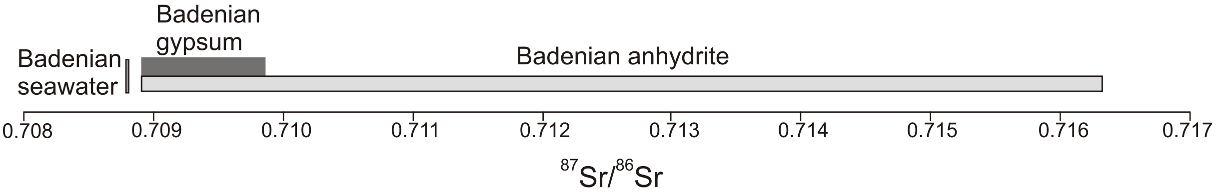

Fig. 9. Ranges of $^{87}Sr/^{86}Sr$ ratios in Badenian gypsum and anhydrite of the Carpathian Foredeep in Poland (Kasprzyk *et al.*, 2007) and Ukraine (this paper)

Contemporaneous, Badenian seawater values after McArthur *et al.* (2001) assuming that the Badenian evaporites of the Polish and Carpathian Foredeep Basin were formed between 13.81 and 13.5 Ma (*cf.* Bukowski *et al.*, 2010; de Leeuw *et al.*, 2010)

of solutions to which the strontium is released (Bain and Bacon, 1994, with references therein).

The $^{87}Sr/^{86}Sr$ ratios of minerals in marine, bedded evaporite deposits are often higher than that of contemporaneous seawater, which is often explained in terms of secondary origin or recrystallization of these minerals in presence of radiogenic ^{87}Sr-bearing fluids (Chaudhuri and Clauer, 1992; Shields, 2007), mostly from a detrital source material (e.g., Stueber and Pushkar, 1983; Hovorka *et al.*, 2007; Schaefer, 2009). Kasprzyk *et al.* (2007) assumed that the clay intercalations are the source of radiogenic Sr in the sulphate unit, and particularly in anhydrites, but in Mamalyha clay intercalations are very thin and rare, and the gypsum itself contains negligible contents of Fe (0.01–0.06%) and Al (0.01–0.07%); usually the contents of Fe and Al are close to the lower limits of their ranges. Therefore, although relatively slightly radiogenic $^{87}Sr/^{86}Sr$ in anhydrites formed in the halite facies (such as at Selets'-Stupnytsya and Hrynivka) could have been derived from clay intercalations, for interpretation of the Mamalyha highly radiogenic $^{87}Sr/^{86}Sr$ another explanation is needed.

In a pilot study of sulphates from the Badenian of the Polish Carpathian Foredeep Basin, Kasprzyk *et al.* (2007) noticed that the anhydrite samples have more radiogenic $^{87}Sr/^{86}Sr$ ratios than the gypsum samples, and also trend towards higher $\delta^{34}S$ and $\delta^{18}O$ values. The high $^{87}Sr/^{86}Sr$ ratios in the anhydrite samples was interpreted as resulted from the mixing of fluids of two different isotopic signatures, i.e., marine waters and continental waters, during sulphate deposition and diagenesis (Kasprzyk *et al.*, 2007). In particular, interbedded siliciclastic deposits could be important sources of highly radiogenic strontium by simple mixing and interactions between the brines and rocks (Denison, pers. comm., 2007, in Kasprzyk *et al.*, 2007), and the different strontium isotope compositions of gypsum and anhydrite seem to reflect two different hydrological provenances of sulphate formation in the Badenian basin (Kasprzyk *et al.*, 2007). However, although one sample of Badenian primary gypsum (laminated gypsum) from Southern Poland studied by Kasprzyk *et al.* (2007) showed a slightly radiogenic value (0.708915), the other one (selenitic gypsum) had more radiogenic $^{87}Sr/^{86}Sr$ (0.709157, Kasprzyk *et al.*, 2007) that is comparable to the ratios recorded in the upper part of the primary gypsum at Mamalyha. On the other hand, the anhydrite samples from Hrynivka and Selets'-Stupnytsya show $^{87}Sr/^{86}Sr$ ratios very close to the ratio reported by Kasprzyk *et al*. (2007) from laminated clastic, primary gypsum, and thus not necessarily the strontium isotope compositions of gypsum and anhydrite are different, as assumed by Kasprzyk *et al.* (2007; Fig. 9).

High radiogenic $^{87}Sr/^{86}Sr$ ratios in the primary gypsum of the Mamalyha quarry indicate a radiogenic strontium non-marine contribution to the basin, and clearly lower $^{87}Sr/^{86}Sr$ ratios in the upper part than in the lower part of the gypsum sequence of Mamalyha require an explanation. A possibility that this decrease in $^{87}Sr/^{86}Sr$ ratios through time reflects an increase in the distance from high-radiogenic Sr source is not supported by data which suggest the transgressive nature of the Tyras gypsum in the Ukrainian Carpathian Foredeep (Peryt, 2001, 2006). Therefore, we suggest that the recorded higher $^{87}Sr/^{86}Sr$ ratios in the lower part of gypsum sequence reflect a higher proportion of runoff during an initial lowstand situation (*cf.* Rhodes *et al.*, 2002). The lower $^{87}Sr/^{86}Sr$ ratios in the upper part of the gypsum sequence are due to changes in the catchment, either in bedrock or in soils, or both.

Quite common low bromine contents of halite in the rock salt successions of Selets'-Stupnytsya and Hrynivka indicate major recycling during the Tyras deposition; the Hrynivka 525 section (Fig. 3) shows generally lower Br contents than the Selets-Stupnytsya 348 section (Fig. 4). The halite-associated anhydrite in the Hrynivka 525 section shows $\delta^{34}S$ values of 21.6‰ (anhydrite nodule in halite, depth 454 m) and 22.2‰ (anhydrite occurring in salt breccia, depth 342 m; Galamay, 1997) which are similar to $\delta^{34}S$ values of other Badenian anhydrites of West Ukraine (19.7–21.6‰; Kovalevych and Vityk, 1995; Galamay, 1997), Romania (20.3–21.1‰; Galamay, 1997) and Poland (Peryt *et al.*, 2002; Kasprzyk *et al.*, 2007). Taken together, both geochemical markers indicate that although the parent brines were of marine origin, they were subject to significant inflows of meteoric waters (*cf.* Cendón *et al.*, 2004).

The recycling is also manifested in the Mamalyha gypsum. The high $\delta^{34}S$ values in the lower part of the Mamalyha gypsum section may be explained in two ways. The first interpretation follows the concept of Cendón *et al.* (2004) that the high $\delta^{34}S$ values may be the result of recycling of coeval sulphates deposited on the marginal settings. This is in accordance with the common physical recycling shown by the common clastic gypsum within stromatolitic gypsum (Figs. 4 and 6B). In addition, the recorded slight upwards trend towards more marine values of both $\delta^{18}O$ and $\delta^{34}S$ values (Fig. 5) agrees with the overall transgressive nature of the Badenian gypsum (Peryt, 2001, 2006). In addition, the oxygen, sulphur and strontium isotopic compositions of the gypsum display an upsection decrease while the strontium content increases (Fig. 5). In the Gulf of Carpentaria (N Australia) non-marine evaporites formed at about 70 ka show a similar trend as far as the oxygen and sulphur isotopic compositions and the strontium content (Playà *et al*., 2007) are concerned, but the $^{87}Sr/^{86}Sr$ ratio increases there also, as opposed to the Mamalyha section. The oxygen and strontium isotopic compositions of the Carpentaria gypsum display a slight positive covariance which is interpreted by Playà *et al*. (2007) as due to an increase in continental input probably associated with dissolution of previously deposited gypsum with rising water level in Lake Carpentaria. The strontium isotope dataset of the Mamalyha gypsum is certainly too small to allow for testing the correlation among $\delta^{34}S$, $\delta^{18}O$ values and Sr isotopes within individual gypsum samples, especially because a part of the strontium isotope analyses was done on another sample set than the sulphur and oxygen isotope analyses. However, it seems clear that high $\delta^{18}O$ values are characteristic of the part of the Mamalyha section showing higher $^{87}Sr/^{86}Sr$ ratios, thus supporting the importance of evaporite recycling in the Mamalyha geochemical record. Although clearly the sulphur and strontium isotopes had different mechanisms for their increase (e.g., Lu *et al.*, 2001; Lu and Meyers, 2003), both can be related to the dissolution of previously deposited gypsum during the rise of Badenian water level (*cf*. Playà *et al.*, 2007).

The second possibility is that the high $\delta^{34}S$ values resulted from prolonged stratification and an efficient “sulphur pump” operation, as envisaged for the hypersaline Lake Lisan (Torfstein *et al.*, 2005). However, the Mamalyha gypsum originated in the very low relief, coastal salina system strongly affected by inflow of continental water (Peryt, 1996). This inflow is inferred based on regional premises indicating a salinity gradient decrease toward the land (Peryt, 1996) as well as because of the occurrence of clayey and marly intercalations (Bąbel *et al.*, 2009) and the common intercalations of clastic, laminated gypsum (Peryt, 1996; Bąbel *et al.*, 2009). Therefore, it seems that a conceptual model describing the sulphur cycle under the particular limnological-geochemical configuration of Lake Lisan has no application to the Badenian Carpathian Foredeep Basin.

CONCLUSIONS

1. Highly radiogenic $^{87}Sr/^{86}Sr$ ratios (from 0.709154 to 0.709838) in Badenian primary gypsum of the Mamalyha gypsum (West Ukraine) show a major non-marine contribution to the basin. There is a general decrease of $^{87}Sr/^{86}Sr$ ratios up the Mamalyha gypsum section.

2. The high radiogenic $^{87}Sr/^{86}Sr$ ratios in the Mamalyha gypsum section are accompanied by increased $\delta^{18}O$ and $\delta^{34}S$ values. The high $\delta^{34}S$ values resulted from recycling of coeval sulphates deposited on the marginal settings. The upwards trend towards more marine values of both $\delta^{18}O$ and $\delta^{34}S$ values agrees with the overall transgressive nature of the Badenian gypsum.

3. Halite facies-associated anhydrite from the Selets’-Stupnytsya 348 and Hrynivka 525 boreholes shows very similar $^{87}Sr/^{86}Sr$ ratios (0.708902 and 0.708917, respectively) that are higher than the ratio of the Badenian contemporary seawater (0.708800–0.708809) but considerably lower than the ratios of the Mamalyha gypsum section. Although the dataset is certainly too small to validate the assumption conclusively, the concept of different strontium isotope compositions of gypsum and anhydrite, and hence two different hydrological provenances of sulphate formation, in the Badenian basin should be treated with caution. It seems that both primary gypsum and anhydrite show high radiogenic $^{87}Sr/^{86}Sr$ ratios in the Badenian, and the range of $^{87}Sr/^{86}Sr$ ratios for gypsum overlaps with a part of the range of the $^{87}Sr/^{86}Sr$ ratios for anhydrite.

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