Sulphur isotopic composition of K–Mg sulphates of the Miocene evaporites of the Carpathian Foredeep, Ukraine

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Abstract: Miocene evaporites of the Carpathian Foredeep host an interesting sulphates group of potash deposits, including about 20 sulphates minerals. The study of sulphur isotopic composition of 10 of the sulphates minerals from the Kalush–Holyh and Stebnyk potash deposits shows that only the basal Ca-sulphates (anhydrite) from the Kalush–Holyn potash deposits has $\delta^{34}S$ values typical of Neogene marine evaporites (+21.0‰). Potash minerals related to the deposits (polyhalite, anhydrite, kainite, langbeinite and kieserite) show $\delta^{34}S$ values from +15.28‰ to +17.54‰, and the weathering zone minerals (picromerite, leonite, bloedite, syngenite and gypsum) show values ranging from +14.73‰ to +18.22‰. The recorded depletion of sulphur isotopic composition of the salt minerals of potash deposits (and their weathering zone) was probably caused by one or more of the following isotope fractionation factors: bacterial reduction of sulphate, effect of crystallization and inflow of surface waters containing sulphates enriched in light sulphur isotopes due to pyrite oxidation. Accordingly, the observed sulphur isotopic composition of minerals from these potash deposits demonstrates the depletion of the original brines and continual inflow of new (concentrated) seawater. Similar sulphur isotopic composition of minerals from the potash deposits and their weathering zone points out that there was no significant sulphur isotope fractionation during weathering and in this case inflow of surface water has an insignificant influence on sulphur isotopic composition.

Miocene K–Mg sulphates in the Ukrainian part of the Carpathian Foredeep basin have been mined since the mid-nineteenth century (Korenevskiy & Donchenko 1963, with references therein) and their economic importance has led to intensive mineralogical, petrographical and geochemical studies aiming to explain the composition and origin of these potash deposits. Present concepts on the origin of K–Mg salts strongly stress a very shallow water, marginal marine sedimentary environment, in the decimetre range of brine depth, and such a concept was earlier applied to the Miocene potash in the Carpathian foredeep basin of the Ukraine (e.g. Valyashko 1962). However, on the basis of physicochemical considerations, many authors considered that Lower Miocene potash salts were formed in a deeper setting (e.g. Kovalevich 1978; Petrichenko 1988; Peryt & Kovalevich 1997).

During the extensive study of the Miocene K–Mg sulphates in the Ukrainian portion of the Carpathian Foredeep (see Hryniv *et al.* 2007), particular attention was paid to the K–Mg sulphates of the Stebnyk and Kalush–Holyn deposits (Figs 1–4). Despite having a somewhat different stratigraphical position, both deposits show the same mineralogical characteristics (e.g. Kovalevich 1978; Griniw 1994). K/Ar dating of the potassium–magnesium sulphate minerals from both deposits provided evidence that they have recrystallized at roughly the same time, and this recrystallization was apparently the response to three major tectonic events that affected the area (Wójtowicz *et al.* 2003). However, despite the intensive geochemical research, no isotope geochemical study for those deposits has been reported and the aim of this paper is to fill that gap in our knowledge. It should be mentioned that, as noted by Raab & Spiro (1991), data on late evaporative facies are rare. Their experimental data showed that primary, unaltered, highly evaporated minerals can have *c.* 2‰ depletion value, relative to the first gypsum, by the simple mechanism of a continual evaporation process (Raab & Spiro 1991). Strauss (1997) commented that there is isotopic depletion in ^{34}S (by as much as 4‰) of late-stage sulphate, deposited within the halite and potash–magnesia facies.

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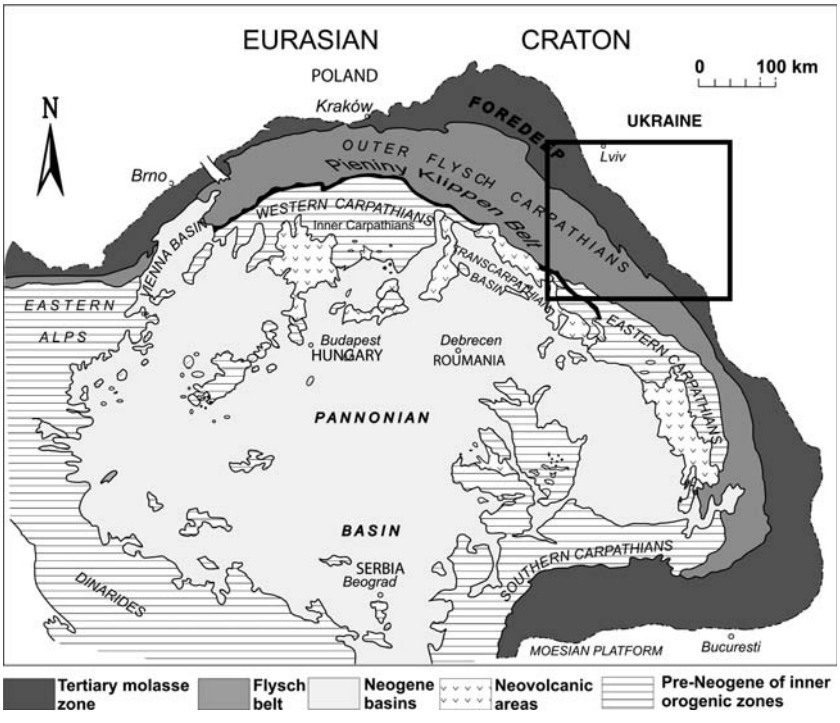

Fig. 1. Geological map of the Carpathian–Pannonian basin system (after Kovač *et al.* 1998) showing the location of Figure 2 (rectangle).

Geological setting

The Carpathian Foredeep basin was formed in the early Miocene, northeast of the overthrusting Carpathian nappes. The basin is filled with Miocene deposits (mostly siliciclastic and minor evaporites) that are more than 3000 m thick in the area adjacent to the Carpathians (Oszczypko *et al.* 2006). In the Ukrainian part of the foredeep, three tectonic zones are distinguished: the outer (Bilche-Volytsa), a central (Sambir Nappe thrust over the foreland) and an inner (Boryslav-Pokuttya Nappe, thrust over the Sambir Nappe and the underlying foreland). The Stebnyk potash deposit is located in the latter zone, near the front of the overthrust Carpathian nappes, and the Kalush potash deposit is located in the central zone (Fig. 2). Because of this geological location, the stratigraphic section is most likely a repeated section (Fig. 3).

The Stebnyk potash deposit is part of the Vorotyshcha suite (Fig. 4). In this paper, instead of *formation*, the term 'suite' is applied, which is more consistent with its poorly defined and complex stratigraphy. The Vorotyshcha suite is composed of three members: a lower salt-bearing, a middle terrigenous and an upper salt-bearing one, with a total thickness more than 2000 m (Petryczenko *et al.* 1994), but new interpretation assumes that upper and lower salt-bearing members belong to the same, Vorotyshcha suite, and that the terrigenous member separating them is an olistostrom (Kulchitsky 1986; Koriń 1994). The occurrence of multiple potash layers and the great thickness of the suite are the result of intensive folding and overthrust tectonics and the normal total thickness of potash deposits in Stebnyk is actually 10–125 m (Dzhinoridze 1980; Koriń 1994; Peryt & Kovalevich 1997). There is only one potash complex (langbeinite–kainite) in the middle part of the suite (Koriń 1994). The complex consists of beds of kainite, langbeinite and kainite–langbeinite (with sylvite and kieserite). Polyhalite beds (5–15 cm thick) occur at the base and the top of the potash complex (Koriń 1994). The mineralogical composition of individual parts of the mined horizons varies considerably (see Kovalevich 1978), but the bulk chemical composition (as far as Mg, K_2 and SO_4 are concerned) is constant. The actual, unfolded thickness of the potash complex is probably less than 15 m. The micropalaeontological data indicate the Early Miocene Eggenburgian age of the Vorotyshcha suite (Andreyeva-Grigorovich *et al.* 1997; Fig. 4). The Vorotyshcha suite is overlain by the Stebnyk suite, a molasse deposit with

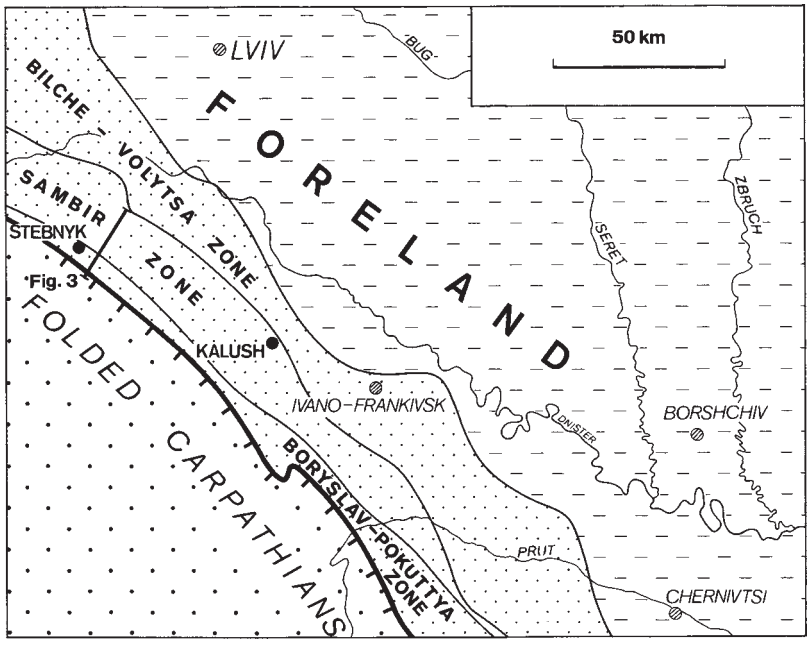

Fig. 2. The main tectonic units of West Ukraine (after Vul *et al.* 1998). The Carpathian Foredeep area is indicated by the fine stripple; adjacent Folded Carpathians and Transcarpathian Depression (SW of the Carpathian Foredeep) are indicated by the coarse stripple, and the Carpathian Foreland area (NE of the Carpathian Foredeep) is indicated by dashed lines.

graded bedding formed from relatively shallow subaqueous turbidite currents as well as from subaerial debris flows (Kulchitskiy 1986, p. 14).

The lithostratigraphical and chronostratigraphical position of evaporite deposits in the Kalush–Holyn deposit is subject to continuing controversy (Fig. 4; see Wójtowicz *et al.* 2003, for review). The potash-bearing sequence consists of interbedded salt claystones, breccias, potash and rock salt, up to 500 m thick (Petryczenko *et al.* 1994). The present structure of the Kalush–Holyn deposit is complex but it seems that during sedimentation in the evaporite basin only two beds of potash salts were formed: the lower chloride and upper sulphate (Dzhinoridze 1973; Griniw 1994). The unfolded thickness of this sulphate potash complex is 38.5 m (Griniv 1985). The major rock-forming minerals of the potash deposits are halite, langbeinite and kainite. Kieserite, polyhalite, anhydrite, sylvite and carnallite are present in

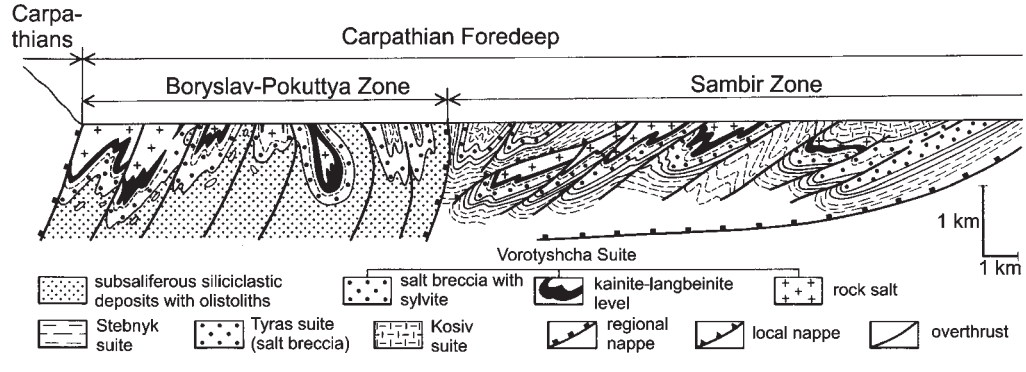

Fig. 3. SW–NE geological cross-section through the inner and central zones of the Carpathian Foredeep (after Koriń 1994); the cross-section line is shown in Figure 2.

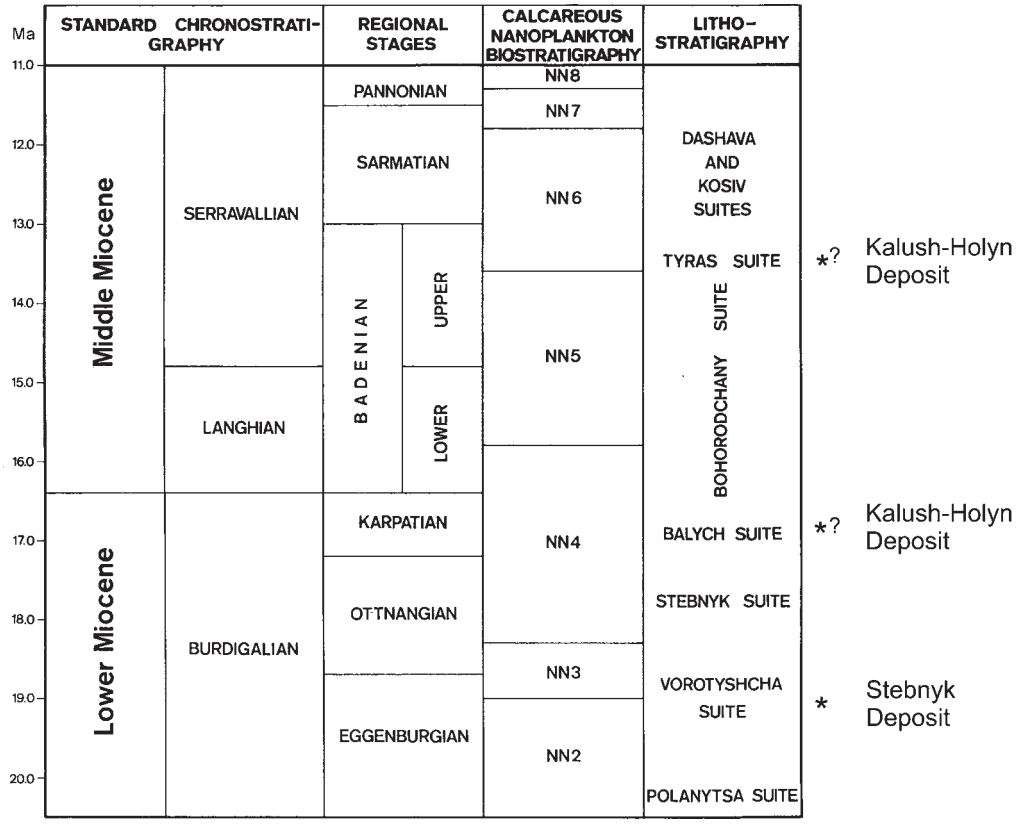

Fig. 4. Stratigraphic position of the Kalush–Holyn Deposit (two interpretations marked by asterisks) and the Stebnyk Deposit in the Miocene of the Ukrainian part of the Carpathian Foredeep. Chronostratigraphy after Rögl (1996), Vakarcs *et al.* (1998) and Steininger & Wessely (2000); lithostratigraphy after Petryczenko *et al.* (1994).

smaller quantities. Both the tectonic structure and the composition of potash rocks of the Kalush–Holyn and the Stebnyk deposits show similarities. Evaporite deposits in the Kalush–Holyn area are included within the Dombrovo suite (Dzhinoridze 1973) and are counterparts of the Badenian Tyras suite (Dzhinoridze 1980). The Badenian age of this deposit is supported by the study of calcareous nannoplankton assemblages, suggesting that the evaporites in the Kalush deposit belong to the NN6 Zone (Andreyeva-Grigorovich *et al.* 2003), similar to the Badenian evaporites of Poland (Peryt 1997), but geochemical arguments and radiometric data suggest that the Kalush evaporites can be Karpatian in age (see Wójtowicz *et al.* 2003, for discussion).

Mineralogical characteristics

Primary deposited minerals (Table 1) in the Miocene salt basins were halite, epsomite, sylvine, hexahydrite and possibly kainite. During deposition of the potash, the brines were at the sylvite stage of concentration as indicated by a limited occurrence of carnallite, chemical composition of inclusion fluids and the bromine content in halite (Kovalevich 1978; Petrichenko 1988). During early diagenesis, metastable minerals reacted among themselves and with brine and thus new minerals formed: stable (kainite) or metastable (tetra- or pentahydrate of Mg sulphate). There is a deficit of calcium during the potash stage and therefore the polyhalite can be formed only when the calcium is delivered by the (concentrated) seawater. Although the polyhalite crystallization is possible, as indicated by experimental data, it is more probable that the polyhalite was formed due to chemical reaction of the precipitated gypsum with potassium- and magnesium-bearing brines (Valyashko 1962). Under burial conditions, due to the temperature increase, dehydration and recrystallization, the formation of new minerals took place. The most important changes of composition, structure and texture of

Table 1. *Minerals discussed in this paper and their chemical composition*

Anhydrite	$CaSO_4$
Bloedite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$
Gypsum	$CaSO_4 \cdot H_2O$
Halite	NaCl
Kainite	$KMg(SO_4)Cl \cdot 3H_2O$
Kieserite	$MgSO_4$
Langbeinite	$K_2Mg_2(SO_4)_3$
Leonite	$K_2Mg(SO_4)_2 \cdot 4H_2O$
Picromerite	$K_2Mg(SO_4)_2 \cdot 6H_2O$
Polyhalite	$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$
Sylvite	KCl
Syngentite	$K_2Ca(SO_4)_2 \cdot H_2O$

evaporites of the Carpathian Foredeep are related to overthrusting of Carpathian nappes and the resulting regional overheating that resulted in the major recrystallization phase of the rocks (cf. Wójtowicz *et al.* 2003).

There also exists another possible model of deposition of evaporites in the Carpathian Foredeep, one that assumes a possibility of precipitation of kainite and langbeinite from brines due to the density- and temperature-stratification of the water (the bottom brines had temperature >45 °C according to Petrichenko 1988, pp. 103–106).

During the uplift of this area, when evaporites became subject to dissolution by surface waters, the clay–gypsum cap began to form. In its lower part, at the boundary with potash rocks, a discontinuous bed and lenses occur that are composed of weathering zone minerals (a schoenite cap, Lobanova 1956).

Materials (sampling)

For the sulphur isotope study we sampled the potash zone and the adjacent polyhalite–anhydrite rock (from mine and open-pit surfaces) occurring at the boundary between the potash zone and salt breccia (seven samples from the Stebnyk deposit and 13 samples from the Kalush–Holyn deposit). In addition, two samples of anhydrite from the Kalush–Holyn deposit were taken (basal anhydrite and anhydrite from the salt breccia with carnallite) and seven samples of minerals from the lower part of the cap rock of the Dombrovo quarry. In total 29 samples of 10 minerals have been analysed: anhydrite, four minerals of the potash zone and five minerals from the cap rock.

Anhydrite forms a basal bed (0.8 m thick in the sampled area) of the Kalush salt sequence (such a basal anhydrite is lacking in the Stebnyk deposit), and it is commonly present within the polyhalite–anhydrite beds (0.01–0.3 m thick) that occur at the contact of the potash zone and salt breccia: anhydrite adjoins this breccia, and polyhalite adjoins the potash zone. One sample of pure gypsum replacing polyhalite from the polyhalite–anhydrite bed was taken and also one sample of anhydrite from the salt breccia with carnallite; anhydrite forms nodules in the breccia. Polyhalite was taken from three varieties of polyhalite rocks: in clayey polyhalite rock from the potash zone, where it forms beds rich in clay (25%) that are typically 5–10 cm thick and grey in colour; in the red variety of pure polyhalite (with beds 1–3 cm thick), in complexes up to 2 m thick, which are characteristic for places where the potash zone disappears laterally; and in polyhalite in the polyhalite–anhydrite beds. In four cases both anhydrite and polyhalite were sampled from the same bed (samples 84 and 95, 89 and 94, 85 and 97, and 88 and 92). Kainite rock is the most common potash rock in the Ukrainian part of the Carpathian Foredeep. It is bedded, consisting of alternation of pure kainite (yellow in colour) and clayey kainite (yellow-grey in colour); the samples were taken from the pure variety of kainite rock. Langbeinite occurs in the form of langbeinite rock that contains small admixtures of halite, polyhalite and clay material (Lobanova 1956). Kieserite was taken from the kainite–langbeinite rock that also contains sylvite and water insoluble residue; we selected pure kieserite.

From the middle part of the cap rock of the Dombrovo quarry we selected samples of monomineralic crystals of gypsum and syngenite, and from the lower part of the cap rock leonite, picromerite and bloedite.

Methods

Each sample was powdered in the agate mortar, then *c*. 100 mg of the powder was dissolved in distilled hot water. After complete dissolution of sulphates, the solution was filtered and $BaSO_4$ was precipitated by adding $BaCl_2$ solution acidified with HCl. The precipitate was washed by distilled water until the chlorides had been removed, and dried. $BaSO_4$ powder was additionally purified by heating in an electric oven at a temperature of about 500 °C. Pure barium sulphate was then treated with chemical procedure in a vacuum line to obtain SO_2 gas for isotope analysis. We employed this method where SO_2 was extracted by quantitative reduction of $BaSO_4$ using $NaPO_3$ (Halas & Wolacewicz, 1981; Halas & Szaran, 2001). The sulphur isotopic composition was analysed on a dual inlet and triple collector mass spectrometer (reconstructed MI 1305) in the Institute of Physics of the Maria Curie–Sklodowska University

in Lublin. Precision of the spectrometer measurements was 0.05–0.08‰ and reproducibility of the chemical procedure about 0.15‰. Obtained results as a conventional delta notation were normalized to the CDT by analysis of the NBS-127 standard.

Results

Results of our analysis are shown in Table 2. The range of $\delta^{34}S$ values for anhydrite, polyhalite and gypsum from the Stebnyk deposits is relatively small (15.28–16.73‰), and both the minimum and maximum values characterize the polyhalite beds within the potash zone. When one polyhalite–anhydrite bed was examined, anhydrite showed a lower $\delta^{34}S$ value (15.75‰) than polyhalite (16.60‰); in turn, when gypsum replaces polyhalite, gypsum shows lower a $\delta^{34}S$ value (15.99‰) than anhydrite (16.11‰).

In the Kalush–Holyn deposit, basal anhydrite shows the highest $\delta^{34}S$ value recorded in the studied sample set (21.00‰). Polyhalite shows a small range of $\delta^{34}S$ values (17.18–17.54‰) and in two pairs of samples that were taken from the same anhydrite–polyhalite bed the $\delta^{34}S$ values for polyhalite are greater than for anhydrite (by 1.59 and 1.60‰, respectively; see Table 2). The $\delta^{34}S$ values for kainite, langbeinite and kieserite as well as red polyhalite are within the range 15.93–17.38‰ (average 16.53‰).

The range of $\delta^{34}S$ values for minerals from the cap rock is 14.73–18.22‰ (average 16.44‰); gypsum and syngenite that were taken from the middle part of the cap rock show smaller $\delta^{34}S$ values (14.73–15.96‰) compared with minerals from the lower part of the cap rock (the $\delta^{34}S$ values of which are 16.57–18.22‰).

Discussion and interpretation

The comparison of isotopic composition of sulphate minerals that originated during various phases of formation of the potash deposits in the Carpathian Foredeep basin indicates that the processes of transformation and recrystallization did not lead to a significant isotopic fractionation of sulphur.

Discussion

The $\delta^{34}S$ values of basal anhydrite indicate the marine provenance of parent water (cf. Paytan *et al.* 1998). The polyhalite–anhydrite beds occurring at the transition zone between the potash zone and the salt breccia zone were formed during diagenesis. The study of pore waters in the Stebnyk deposit indicated that the brines in the potash zone are buried sulphate brines (that were characteristic for the phase of potash deposition) and the brines in breccia zone are Ca chloride brines (Valyashko *et al.* 1974). The latter brines are modified due to interaction of buried sulphate brines with clay minerals that supplied Ca ions to the brines, and this led to the brine losing the sulphate ion (Valyashko 1962). The polyhalite–anhydrite beds were formed at the geochemical barrier between those two types of brines, and both anhydrite and polyhalite are newly formed minerals (*de novo*). Of those two minerals, polyhalite was the first to crystallize and it consumed available potassium and magnesium ions, so that further crystallization of the brine led to precipitation of anhydrite. Accordingly, the $\delta^{34}S$ values recorded in anhydrite from polyhalite–anhydrite beds are lower than they are in polyhalite due to the effect of fractionation during crystallization.

The $\delta^{34}S$ values for the minerals from the cap rock vary within a slightly wider range. However, gypsum and syngenite that are related to the middle part of the cap rock show lower values than those characterizing the potash zone. In turn, minerals from the lower part of the cap rock show slightly higher values (17.25‰ on average) compared with the potash zone. The differentiation can be related to the inflow of surface water and the crystallization of new minerals in more open conditions.

Interpretation

These potash deposits are regarded as a lowstand deposit (Peryt & Kovalevich 1997). The bromine content in halite is very close to that characteristic of marine salt (Bilonizhka 1970, 1975; Kovalevich 1978) and the composition of brines inferred from study of fluid inclusions also suggests a dominantly marine origin for these brines (Kowalewicz 1994). The envisaged scenario presented by Peryt & Kovalevich (1997) assumes that the Lower Miocene salts originated by evaporation of mostly marine parent waters that were syndepositionally recycled. During periods of reduced supply of detrital material by inflow, brines in the basin could reach sylvite-saturation level and potash chlorides and sulphates were deposited at that time. Inflow of new brines concentrated in Na and Cl served as a source for halite beds within the potash complex. These beds were formed by mixing of the new brines with bottom brines concentrated to K and Mg salt precipitation. Then the evaporation resulted in decline of the upper level and increase of the bottom brine density, which in turn led to potash precipitation. The multiple complex of such processes led to the origin of the potash complex composed of interbedded potash

Table 2. *$\delta^{34}S$ values of sulphate minerals from the Kalush–Holyn and Stebnyk potash deposits of the Carpathian Foredeep (asterisks in the 'Remarks' column indicate that samples have been taken from the same polyhalite–anhydrite bed)*

Sample	Sample description	Locality	$\delta^{34}S$(‰)	Remarks
Stebnyk Deposit				
70	Clayey polyhalite rock	Stebnyk mine	16.73	
77	Red polyhalite rock	Stebnyk mine	15.28	
83	Polyhalite from polyhalite–anhydrite beds	Stebnyk mine	16.48	
84	Polyhalite from polyhalite–anhydrite beds	Stebnyk mine	16.60	*
89	Gypsum replacing polyhalite from polyhalite–anhydrite beds	Stebnyk mine	15.99	**
94	Anhydrite from polyhalite–anhydrite beds	Stebnyk mine	16.11	**
95	Anhydrite from polyhalite–anhydrite beds	Stebnyk mine	15.75	*
Kalush-Holyn Deposit				
74	Red polyhalite rock	Holyn mine	17.18	
85	Polyhalite from polyhalite–anhydrite beds	Dombrovo quarry	17.54	***
88	Polyhalite from polyhalite–anhydrite beds	Sivka–Kalushska mine	17.36	****
92	Anhydrite from polyhalite–anhydrite beds	Sivka–Kalushska mine	15.77	****
93	Anhydrite from polyhalite–anhydrite beds	Holyn mine	16.95	
97	Anhydrite from polyhalite–anhydrite beds	Dombrovo quarry	15.94	***
101	Anhydrite with carnallite from salt breccia	Holyn mine	17.88	
102	Basal anhydrite	Sivka–Kalushska mine	21.00	
111	Kainite	Sivka–Kalushska mine	15.93	
112	Kainite	Sivka–Kalushska mine	16.18	
113	Kainite	Holyn mine	17.38	
118	Langbeinite	Dombrovo quarry	15.95	
121	Langbeinite	Dombrovo quarry	16.27	
141	Langbeinite	Dombrovo quarry	17.17	
122	Kieserite	Dombrovo quarry	16.15	
123	Leonite	Dombrovo quarry	16.57	
124	Picromerite	Dombrovo quarry	18.22	
128	Bloedite	Dombrovo quarry	16.77	
129	Bloedite	Dombrovo quarry	17.43	
134	Syngenite	Dombrovo quarry	14.73	
136	Gypsum	Dombrovo quarry	15.41	
137	Gypsum	Dombrovo quarry	15.96	

and halite beds contaminated with terrigenous material (Peryt & Kovalevich 1997).

It seems that 4–5‰ difference between the isotopic composition of sulphur in the K–Mg minerals and the basal anhydrite is too large for the simple evolution of brine composition during the normal evaporation of the Carpathian Foredeep Basin according to a Rayleigh-type effect. A more probable process of isotopic fractionation of sulphur that resulted in such a difference could be bacterial reduction of sulphates in brines, which is the most effective process of isotope fractionation. During deposition of potash minerals the brines were stratified and sulphate-reducing bacteria probably were living at the boundary of brines ('bacterial plate', see Sonnenfeld 1984, p. 105). Isotopically light H_2S produced by bacteria may have been sequestered in the upper bed of brine where it was oxidized to sulphates. Part of the light H_2S probably escaped. This led to the heavier isotopic composition of the lower bed of brine; part of that brine underwent outflow/leakage. When the complete evaporation of the upper brine layer occurred, the stratified system disappeared and only homogenized brine body existed, the precipitation of potash minerals occurred.

This precipitation of potash took place from the brine body that was isotopically lighter because of the uptake of lighter sulphur isotopes that previously dominated the upper brine layer. The process of brine depletion in $\delta^{34}S$ due to bacterial reduction was probably superimposed on fractionation related to crystallization of K–Mg sulphates. It is difficult to estimate the volume of the isotope fractionation related to the more general crystallization of sulphate minerals in the Carpathian Foredeep basin due to their origin in an open system in a dynamic environment with multiple inflows of seawater and the probable outflow of concentrated brines. Raab and Spiro (1991) concluded that, during the precipitation of primary minerals of the Mg– and K–Mg sulphate facies, the fractionation factor for the minerals was different than for the minerals precipitated for the gypsum facies. However, their model is based on an assumption of a finite quantity of sulphate ions. In the case of the Miocene Carpathian Foredeep basin, due to the continual inflow of seawater, the volume of incoming sulphate ions was infinite.

Another mechanism that potentially influenced the recorded ^{34}S depletion in potash salts was the delivery of isotopically lighter sulphates from the adjacent land areas during the deposition of the salts in the Stebnyk basin. More light sulphur isotopic composition recorded in the Stebnyk deposit can be explained by more intensive inflow of surface waters from the Carpathian nappes and/or by the oxidation of a part of pyrite contained in bituminous clays of the Menilite suite that occur in olistoliths of the Vorotyshcha suite (that contain a considerable pyrite content, usually 2.0–4.5%; Lazarenko *et al.* 1962).

Conclusions

Isotopic composition of sulphur in the K–Mg sulphate evaporites occurring in the Lower and (?)Middle Miocene of the Carpathian Foredeep basin shows the overprint of isotopic fractionation processes related to precipitation and sulphate reduction resulting in the minerals of potash deposits that show isotopic depletion in ^{34}S by 3.5–5.7‰ and the minerals of the weathering zone by 2.8–6.2‰. The inflow of surface waters from the Carpathians and olistoliths of bituminous shales (Menilite suite) supplied lighter sulphate, formed due to pyrite oxidation, into the Vorotyshcha evaporite basin, resulting in the depletion in ^{34}S by 0.3–1.9‰ in the polyhalites of the Stebnyk deposit compared with similar varieties of that mineral from the Kalush–Holyn deposit.

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