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Diagenetic gypsum, anhydrite and halite in non-evaporite deposits of Belarus

Anatoliy A. Makhnach

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Abstract The location, morphology, geochemistry and genesis of diagenetic gypsum, anhydrite and halite spread in non-evaporite lithofacies in two different regions of Belarus are discussed in present paper. It is shown that diagenetic anhydrite, gypsum and halite could occur in normal marine, aqueoglacial, volcanogenic–sedimentary deposits in shallow or deep water environment and that the bearing rocks are not associated with the evaporating process. Mechanism of gypsum, anhydrite and halite formation in non–evaporite deposits has been studied in detail.

Keywords *Diagenetic gypsum, anhydrite, halite, Upper Proterozoic, Paleozoic, Northern and Middle Belarus, Prypiac' Trough.*

Anatoliy A. Makhnach [amahnach@igig.org.by], Belarussian Research Geological Exploration Institute, Acad. V. Kuprevich Street 7, 220141 Minsk, Belarus. *Manuscript submitted 4 August 2008; accepted 14 November 2008.*

INTRODUCTION

Diagenetic anhydrite, gypsum and halite are widespread in subevaporite and interevaporite strata of evaporite–bearing basins. Two areas of the territory of Belarus were chosen to demonstrate that the above minerals occur in shallow–water and deep–water normal marine deposits, in aqueoglacial, volcanogenic–sedimentary and other rocks that are not associated with the evaporating process. Their formation was due to the evaporite brine supply into the carbonate and terrigenous sediments from the overlying evaporite basins and strata **(a)** by the reflux of above-bottom bittern, and **(b)** by squeezing of intercrystal bittern. One or other mechanism of the brine supply to deposits underlying evaporites may dominate depending on the basin geological evolution. The crystallization of diagenetic sulfate minerals and halite is caused by mixing of evaporite brines with different mineralization (TDS), fluctuations of brine temperature and reservoir pressure. The sulfur isotopic composition of diagenetic sulfate is inherited from the sulfur composition of overlying parent evaporites, but is slightly heavier due to the bacterial sulfate reduction in the course of the subsurface water–rock interaction. A wide range of the 1,000 · Br/Cl ratio variations for the diagenetic halite testifies to repeated changing and mixing brines of different salinities within subsaliferous and intersaliferous formations. The Ca/(Ca+Mg) values of the diagenetic halite are significantly higher than those of the depositional halite due to dolomitization which supplies Ca into the underground brine.

The evaporating process creates various kinds of products. These are strata of evaporite deposits and a large body of brines formed on the earth's surface, as well as diagenetic minerals that are crystallized beneath the surface from brines penetrating deep in the earth. The first two kinds of products have received more study than the third one. Diagenetic minerals often occurring in non–evaporite rocks are represented mainly by gypsum, anhydrite and halite and can not be considered truly evaporite minerals as the process of their crystallization in the rock pores, cavities and fissures of subevaporite and interevaporite formations is not directly associated with the solar evaporation.

The study of diagenetic gypsum, anhydrite and halite located in the non-evaporite lithofacies may be important for a better understanding of the facies nature of host deposits and of the mechanism of evaporite brine traveling from the surface to the subsurface. Besides, subsaliferous and intersaliferous carbonate and terrigenous strata often contain oil and gas, and the formation of "evaporite" diagenetic minerals essentially influences the rock reservoir properties.

GYPSUM IN THE UPPER PROTEROZOIC, LOWER PALEOZOIC AND LOWER DEVONIAN, NORTHERN AND MIDDLE BELARUS

Geological setting

The northern and middle part of Belarus is situated within the Belarussian Uplift, Latvian and Žhlobin Saddles and Orša Depression (Fig. 1). A depth to the crystalline basement there varies between 300 and 1500 m (Geology … 2001). The pre–Mesozoic sedimentary cover is built mainly by sandstones, siltstones, gravelites, clays with tuff admixture and carbonate deposits ranging from the Riphean to the Middle Devonian (Fig. 2). Upper Proterozoic, Lower and Middle Devonian rocks cover this area continuously but Cambrian, Ordovician and Silurian are common only in the west of the area. In Eifelian, Middle Devonian, an evaporite basin existed there, which is represented in the section as gypsum strata of small thickness (5–20 m).

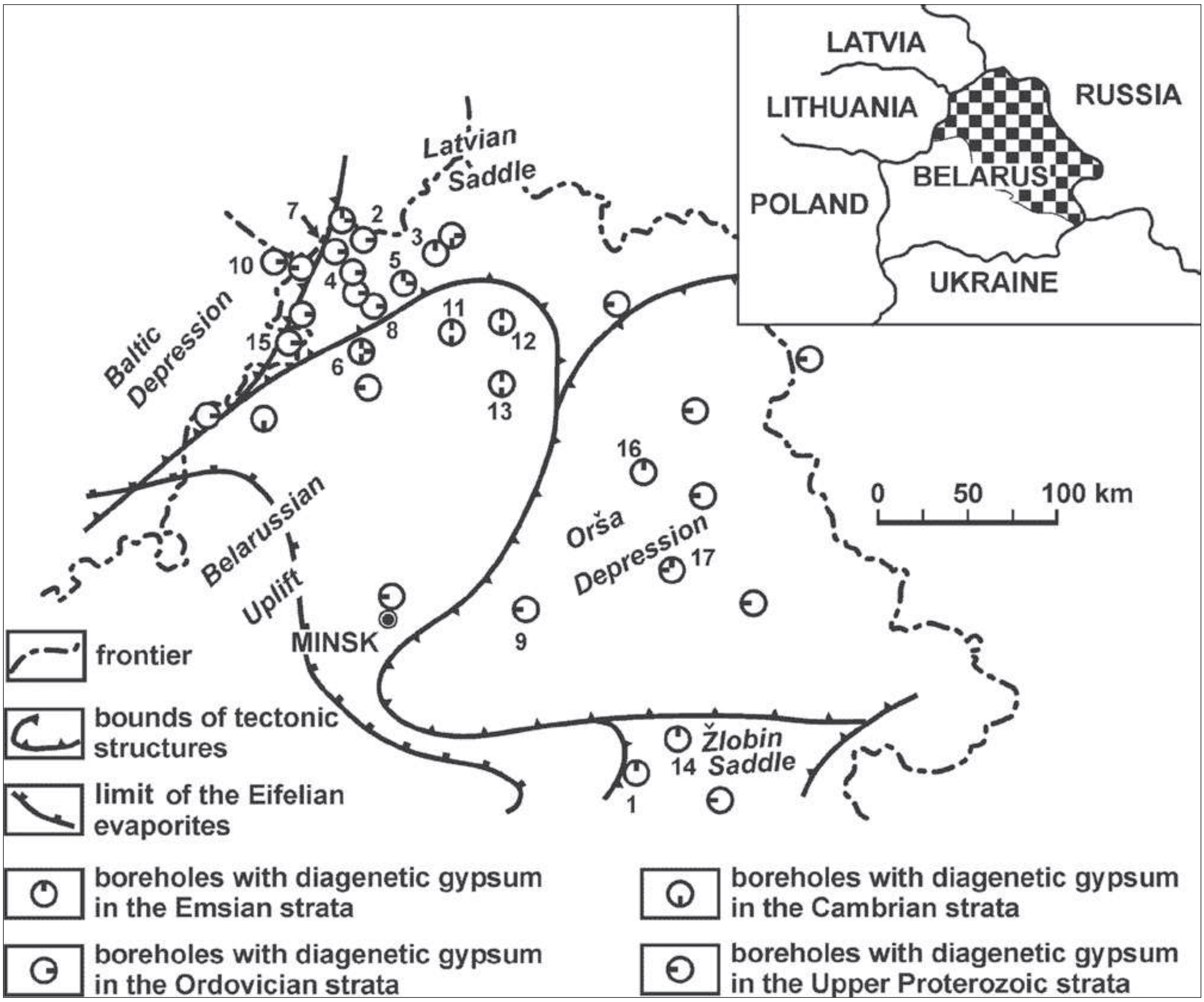

Fig. 1. Spreading of diagenetic gypsum in the Upper Proterozoic to Emsian non-evaporite strata of northern and middle Belarus. Numbers signify boreholes mentioned in Fig. 3 and Table 1: **1** – Balšyja Bortniki 2; **2** – Braslaú 3; **3** – Braslaú 6; **4** – Braslaú 7; **5** – Braslaú 8; **6** – Braslaú 15; **7** – Braslaú 206; **8** – Braslaú 209; **9** – Čherven' 3; **10** – Drukschaj 324; **11** – Liepel' 1; **12** – Liepel' 2; **13** – Liepel' 8; **14** – Aziarany 3k; **15** – Pastavy 5; **16** – Talačyn 26; **17** – Talačyn 38.

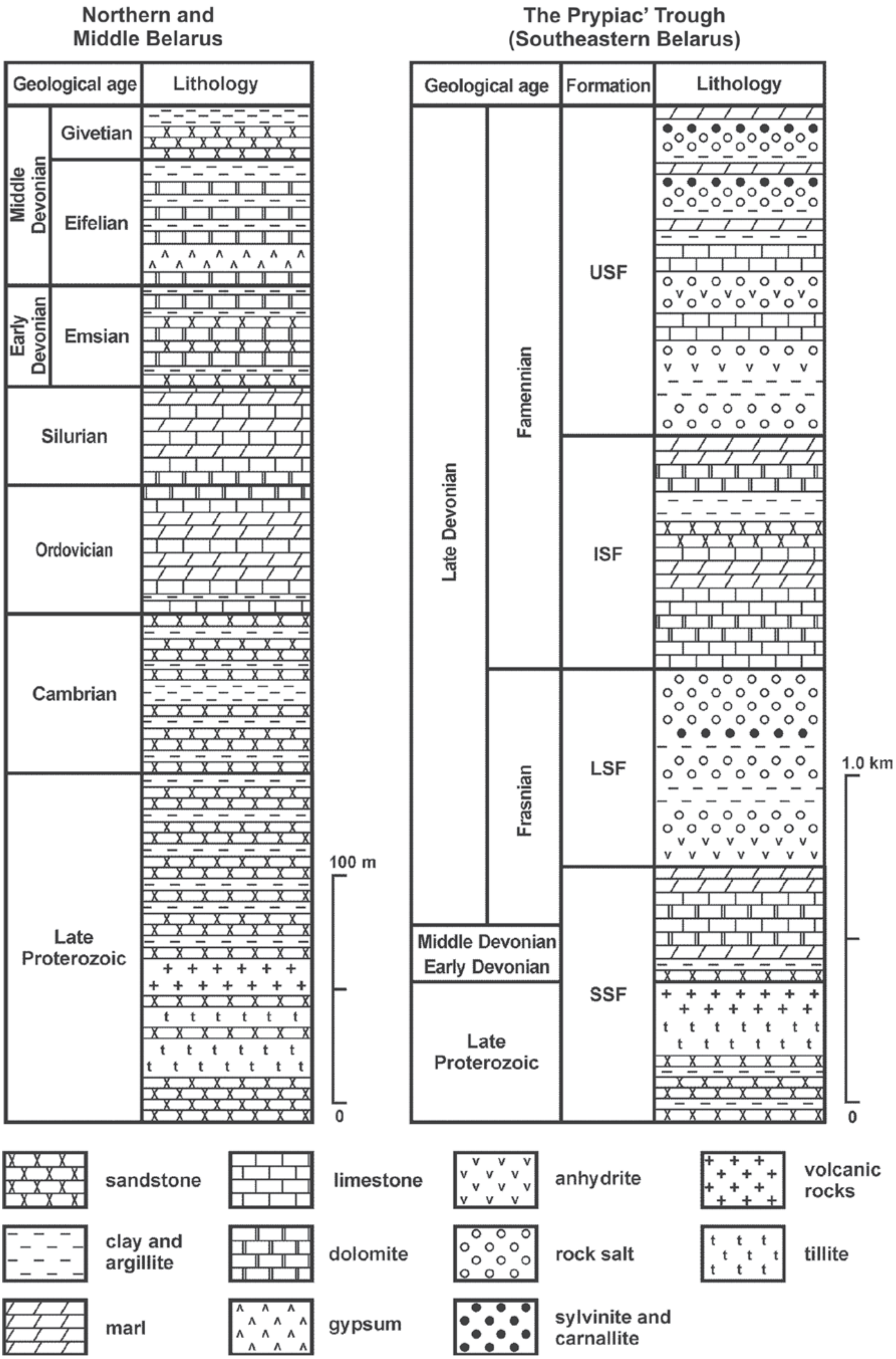

Fig. 2. Highly schematic stratigraphic framework of evaporite and neighbouring units for Belarus with a summary of the main lithologies. SSF is the Subsaliferous Formation, LSF is the Lower Saliferous Formation, ISF is the Intersaliferous Formation, USF is the Upper Saliferous Formation (Geology of Belarus 2001).

Gypsum occurrence conditions and morphology

Numerous diagenetic forms of gypsum were discovered below Eifelian evaporites in Lower Devonian, Ordovician, Cambrian, Vendian and Riphean deposits (see Fig.1). Gypsum is found in these deposits composing the pore, basal, crustificated, poikilitic cement of sandstones, oolitic dolomites, and limestones, and occurs as nests, nodules, filling of fissures and other cavities (Fig. 3).

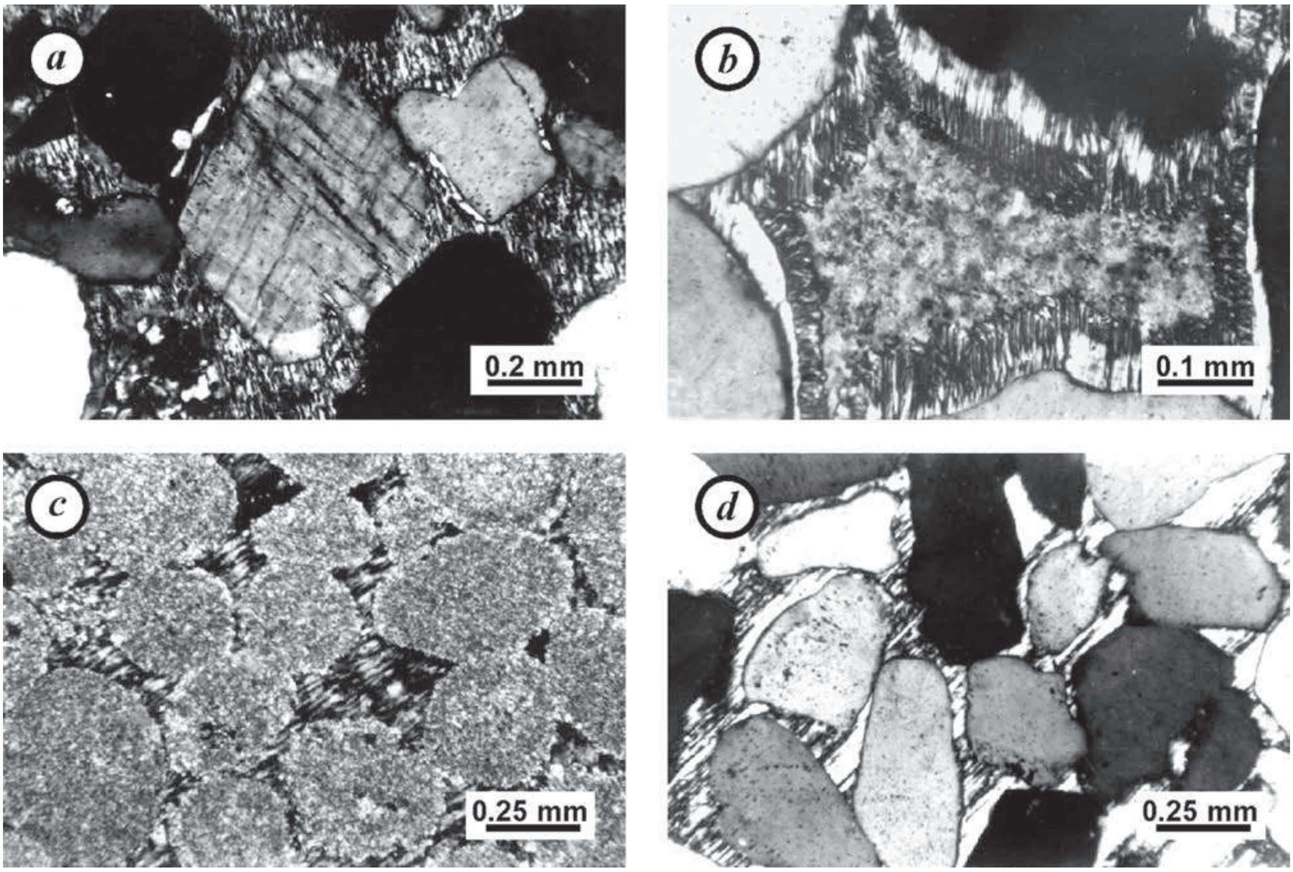

Fig. 3. Cross-polarized photomicrographs of diagenetic gypsum in non-evaporite strata of northern and middle Belarus. **a** – gypsum cement in the Emsian sandstone contacting with regenerated feldspar grane, borehole Liepel' 2, depth 305 m; **b** – gypsum in pore of the Emsian sandstone, note that it is macrocrystalline in the central part of the pore while is fibrous in periphery, borehole Braslaú 3, depth 302 m; **c** – poikilitic gypsum cement in the Emsian pseudo-oolitic limestone, borehole Talačyn 26, depth 406 m; **d** – poikilitic gypsum cement in the Cambrian sandstone, borehole Braslaú 15, depth 220 m.

A diagenetic nature of gypsum is evidently shown by some specific features: (**a**) Gypsum manifestations are not confined to stratigraphic units or facies. It was recorded in almost of all the formations of Ordovician, which rocks are rich in diverse palaeontological remains (brachiopods, bryozoans, corals, cephalopods, trilobites, etc.) suggesting favorable living conditions for shallow–water marine benthos. Gypsum also occurs in Vendian aqueoglacial and volcanic–sedimentary deposits that bear no relation to evaporating process. (**b**) Gypsum is often confined to post–lithification rock features (tectonic fractures, cavities in leached shells, stylolites), which indicates an importance of the hydrogeological factor in the development of the sulfate mineralization. (**c**) Sandstones of Cambrian and Emsian age containing the entire gypsum cement involve products of diagenetic transformation (regeneration of feldspars, glauconitization of clastic grains) that is not possible under conditions of the primary gypsum cementation (Fig. 3a). (**d**) Rather common poikilitic nature of rock cementation suggests a slow growth of crystals most probably under subsurface conditions (Fig. 3b, 3c).

The above data allow assume that the gypsum mineralization in the Lower Devonian, Ordovician, Cambrian and Upper Proterozoic of northern and middle Belarus is due to the action of brines migrated from the overlying Eifelian evaporite basin. This is also supported by the fact that gypsum is absent in Ordovician, Cambrian and Upper Proterozoic formations occurring beyond the limits of an area where Eifelian evaporites are spread (e. g., in the southwest of Belarus).

Sulfur isotope composition of gypsum

One more support of connection between the origin of diagenetic gypsum from the studied deposits and brines of Eifelian halogenesis was provided by the comparative analysis of the sulfur isotope composition of bedded gypsum of Eifelian age and of gypsum manifestations from underlying deposits. The isotope analyses were made at the All-Russian Geological Institute, St. Petersburg (analysts G. M. Efremov and T. V. Ivanova). Calcium sulfates were transformed into cadmium sulfide by reduction with graphite. The SO_2 from sulfides for measuring $^{34}S/^{32}S$ ratio was obtained by oxidation with copper oxide (Ustinov & Grinenko 1965). A precision of determination was ±0.3 ‰.

The sulfur isotope composition of diagenetic gypsum from deposits of the Lower Devonian, Cambrian and Upper Proterozoic was found similar to that of Eifelian bedded gypsum (Table 1). Such a similarity considered in the light of well established sea water $\delta^{34}S$ fluctuation throughout the geological history (Claypool *et al.* 1980) suggests that gypsum in all the studied strata was precipitated from a single solution. This is most clearly demonstrated by a $\delta^{34}S$ value obtained for gypsum from Cambrian deposits, as the sulfur isotopic composition of Cambrian sea water was determined to be the heaviest one in the whole geological history (+30 ‰). Somewhat heavier sulfur isotope composition of gypsum from Lower Devonian, Ordovician and Upper Proterozoic as compared to that of Eifelian gypsum can be easily explained. It is due to the bacterial sulfate reduction of sulfur from brines under subsurface conditions before the diagenetic gypsum crystallization. The bacterial sulfate reduction results, as is known (Kemp & Thode 1968; Zak *et al.* 1980), in the heavier sulfur isotope composition of the residual sulfate in brine, because bacteria utilize predominantly the light isotopes.

Table 1. Sulfur isotopic composition of diagenetic gypsum from the Upper Proterozoic to Emsian non-evaporite sediments in comparison with the Eifelian evaporites, northern and middle Belarus.

Borehole	Depth of sampling (m)	Host rock	$\delta^{34}S$ (‰)
Upper Proterozoic			
Červen' 3	201	Tuffaceous clay	+19.8
Červen' 3	619	Sandstone	+16.3
Liepel' 8	385	Sandstone	+19.9
Talačyn 38	350	Aleurolite	+19.2
Talačyn 38	359	Aleurolite	+19.4
Talačyn 38	361	Sandstone	+16.6
Talačyn 38	366	Sandstone	+18.7
$\bar{x}$ = +18.6 ± 0.6 ‰			
Cambrian			
Braslaú 15	220	Sandstone	+18.0
Drukschaj 324	507	Sandstone	+21.2
Drukschaj 324	584	Gravelite	+22.0
Liepel' 1	349	Gravelite	+20.2
Liepel' 1	353	Gravelite	+21.2
Liepel' 2	335	Sandstone	+18.1
Liepel' 2	337	Sandstone	+15.4
$\bar{x}$ = +19.4 ± 0.9 ‰			
Ordovician			
Braslaú 7	300	Limestone	+19.7
Braslaú 8	306	Dolomite	+18.9

Borehole	Depth of sampling (m)	Host rock	$\delta^{34}S$ (‰)
Braslaú 8	328	Limestone	+15.2
Braslaú 8	330	Limestone	+18.6
Braslaú 15	192	Limestone	+18.2
Braslaú 15	202	Limestone	+18.8
Braslaú 15	209	Limestone	+19.7
Braslaú 206	327	Limestone	+18.7
Braslaú 206	337	Limestone	+19.8
Braslaú 209	291	Limestone	+20.0
$\bar{x}$ = +18.8 ± 0.4 ‰			
Emsian			
Balšyja Bortniki 2	219	Dolomite	+18.0
Balšyja Bortniki 2	219	Dolomite	+19.4
Braslaú 3	287	Sandstone	+16.1
Braslaú 6	327	Sandy breccia	+17.8
Braslaú 8	302	Sandstone	+14.3
Braslaú 15	187	Sandstone	+18.4
Braslaú 15	190	Sandy dolomite	+17.3
Braslaú 15	193	Marl	+18.4
Liepel’ 2	285	Dolomite	+17.8
Liepel’ 2	295	Marl	+19.0
Liepel’ 2	304	Sandstone	+17.8
Liepel’ 8	277	Sandstone	+18.5
Talačyn 26	406	Dolomite	+16.9
Talačyn 26	443	Sandstone	+18.5
Talačyn 38	304	Dolomite	+17.4
$\bar{x}$ = +17.7 ± 0.3 ‰			
Eifelian			
Braslaú 15	178	Bedded gypsum	+16.6
Braslaú 15	182	Bedded gypsum	+15.5
Čherven’ 3	140	Bedded gypsum	+17.3
Liepel’ 1	290	Bedded gypsum	+16.5
Aziarany 3k	216	Bedded gypsum	+17.0
Pastavy 5	226	Bedded gypsum	+17.3
Talačyn 38	297	Bedded gypsum	+17.9
$\bar{x}$ = +16.9 ± 0.3 ‰			

$\bar{x}$ – average value.

ANHYDRITE AND HALITE IN THE INTERSALIFEROUS AND SUBSALIFEROUS DEPOSITS OF THE PRYPIAC' TROUGH, SOUTH –EASTERN BELARUS

Geological setting

The Prypiac' Trough (Fig. 4), a Hercynian palaeorift, contains up to 6–6.5 km thick sedimentary rocks (Geology … 2001). The sedimentary sequence begins with the Subsaliferous Formation which includes Upper Proterozoic and Devonian (Emsian to Frasnian) strata in the western part of the trough and only Devonian deposits in its eastern part (see Fig. 2). The Upper Proterozoic deposits consist of mainly terrigenous sediments being as thick as 450 m. The Devonian part of the Subsaliferous Formation comprises terrigenous and carbonate rocks. Their thickness is 120-300 m. The Subsaliferous Formation is overlain by the Lower Saliferous Formation of Late Frasnian age. The formation is up to 1,100 m thick. The proper salt rock content of the sequence is rather low (47–52 %). The overlying Intersaliferous Formation is represented by Lower Famennian carbonate, terrigenous and volcanogenic rocks (up to 940 m). The Intersaliferous Formation is overlain by the Upper Saliferous Formation of Late Famennian age (300–3,300 m). The Halite Subformation occurs in its lower part. It has the highest salt percentage in the section (up to 75–90 %). The Potassium –Bearing Subformation is distinguished in the upper part of the Upper Saliferous Formation. A concentration of non–saliferous rocks in the sub formation is approximately 50 %.

The chloride type formation brines with high TDS (300–450 g/l) are widespread throughout the Subsaliferous and Intersaliferous Formations (Geology … 2001).

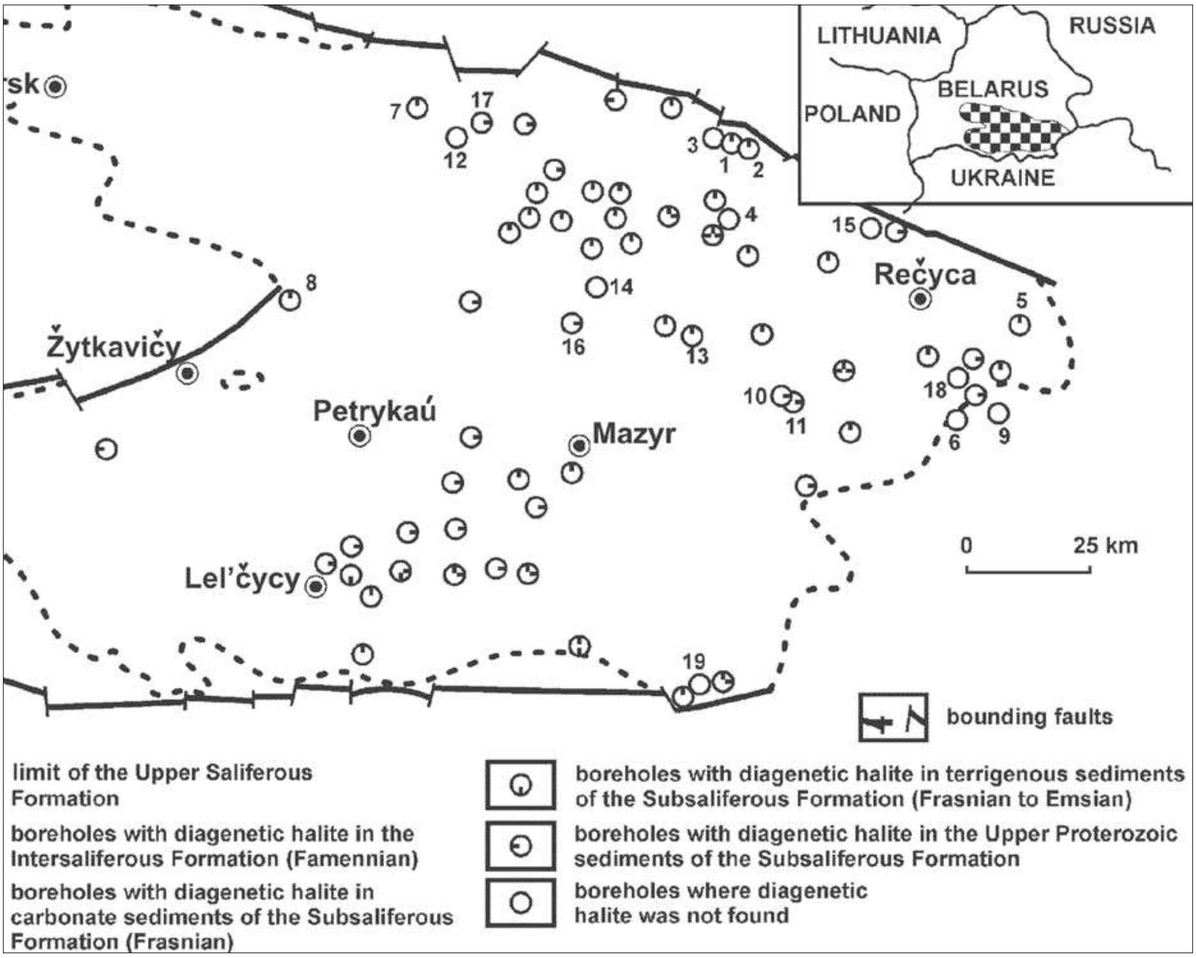

Fig. 4. Spreading of diagenetic halite in non-evaporite strata of the Prypiac' Trough. Numbers signify boreholes mentioned in Fig. 5 and Table 2: **1** – Biarezina 3; **2** – Biarezina 10; **3** – Biarezina 24; **4** –Baraviki 2; **5** – Barščoúka 5; **6** – Eastern Siamionaúka 1; **7** – Chalopieničy 1; **8** – Kuz'mičy 1; **9** – Lojeú 2; **10** – Makanavičy 1; **11** – Makanavičy 2; **12** – Malyn 6; **13** – Navinki 1; **14** – Navasiolki 1; **15** – Peršamajsk 21; **16** – Savičy 9; **17** – Southern Azemlia 1; **18** – Vetchin 8; **19** – Žalon' 2.

ANHYDRITE OCCURRENCE CONDITIONS AND MORPHOLOGY

Newly formed anhydrite is abundant in the Devonian intersaliferous and subsaliferous strata and in the underlying Upper Proterozoic deposits. Sulfate minerals in these sedimentary complexes are not confined to any particular facies, and their distribution is of regional character. The diagenetic anhydrite cement was noted in Riphean marine deposits and Vendian aqueoglacial rocks. Anhydrite is found in all the stratigraphic units of the subsalt and intersalt Devonian and occurs in deposits of various facies (shallow and deep shelf, rather deep –sea, delta front and volcanic –sedimentary ones) and is confined to all type rocks: dolomites, limestones, argillites, sandstones, tuffs, tuffites. A universal occurrence of anhydrite is clearly evidencing their diagenetic nature and the absence of link between its formation and the facies conditions of the host deposit accumulation.

Anhydrite infills cavities, pores, tectonic fissures, cement breccias fragments, clastic and oolitic rock matrix, composes isometric nests (Fig. 5a, 5b). It is represented by accumulations of rather coarse colum-

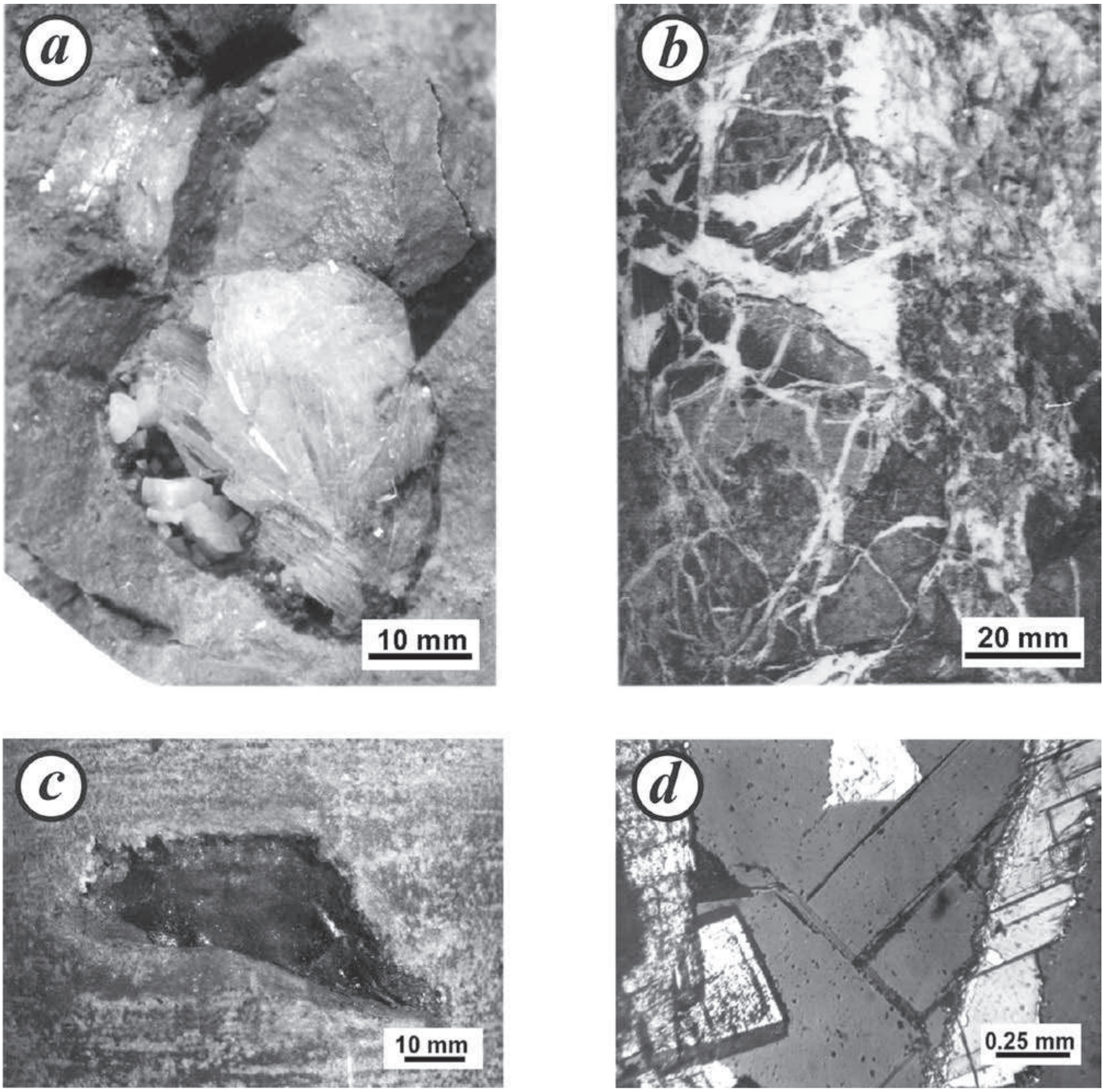

Fig. 5. Petrography of diagenetic anhydrite and halite in carbonate rocks of the Subsaliferous (SSF) and Intersaliferous (ISF) Formations of the Prypiac’ Trough. **a** – core photograph of macrocrystalline anhydrite associated with dolomite in the cavern formed under brachiopod shell dissolution, borehole Chalopieničy 1, ISF, depth 2314 m; **b** – core photograph of tectonic breccia cemented with anhydrite, borehole Barščoúka 5, ISF, depth 3032 m; **c** – core photograph of halite filled a cavern, borehole Savičy 9, SSF, depth 3370 m; **d** – half-cross-polarized photomicrograph of halite in a cavern associated with diagenetic anhydrite and dolomite, borehole Savičy 9, SSF, depth 3210 m.

nar, tabular and acicular crystals, more seldom, by fine-crystalline aggregates. Anhydrite is often associated with normal marine fauna remains or evidences of their former presence, which is indicative of a geochemical contradiction between the "brine" conditions of the diagenetic mineral formation and the normal marine environment of the host sediments accumulation.

Anhydrite was crystallized as a rule after diagenetic dolomite and in filled cavities and fissures incrusted with dolomite. Sometimes, these minerals were formed simultaneously, or dolomite was the last.

Sulfur isotope composition of anhydrite

We have studied the sulfur isotopic composition of diagenetic anhydrite from non–evaporite deposits in comparison with bedded (primary) sulfates from overlying evaporites in the Prypiac' Trough like in the earlier studied case with diagenetic gypsum within northern and middle Belarus. The sulfur isotope composition of diagenetic anhydrite from the Subsaliferous and Intersaliferous Formations of the Prypiac' Trough is given in Table 2. The analyses were made at the All-Russian Geological Institute (St. Petersburg) using above described methods. The $\delta^{34}S$ values of bedded sulfates from the Lower Saliferous (Frasnian) and Upper Saliferous (Famennian) Formations are +24.4±1.8 ‰ and 26.4±0.2 ‰, respectively (Makhnach *et al.* 2005). As in the case with gypsum the $\delta^{34}S$ values of diagenetic anhydrite were found to be somewhat higher than those obtained for the bedded sulfates. This is due to the partial bacterial reduction of sulfate sulfur of evaporite brines that migrated to the reduction environment of deposits underlying evaporite strata.

It should be noted that the similar trend is observed in the other basins with evaporites. $\delta^{34}S$ values of diagenetic anhydrite from the Jurassic carbonate deposits of the Amudarja Basin are +18.2 to +28.2 ‰; these are much higher than the same values of the overlying bedded anhydrites (+13.5 to +17.7 ‰) (Belenitskaya *et al.* 1981). $\delta^{34}S$ of the anhydrite cement of the dolomites from the Nisku Formation in the Alberta Basin (+24.8 ‰) is higher than that obtained for the bedded anhydrite found within this territory (+20.0 ‰) (Nahnybida *et al.* 1982).

Thus, the heavier sulfur isotopic composition of diagenetic sulfates as compared with that of the bedded (sedimentary) sulfates may be used to identify them, which is not always possible with petrography methods used.

Table 2. Sulfur isotopic composition of diagenetic anhydrite from the Upper Devonian non-saliferous sediments of the Prypiac' Trough (southeastern Belarus).

Borehole	Depth of sampling (m)	Host rock	$\delta^{34}S$ (‰)
Frasnian (Subsaliferous Formation)			
Biarezina 10	2529	Dolomite	+29.9
Kuz'mičy 1	1690	Dolomite	+21.4
Makanavičy 1	3572	Dolomite	+29.5
Makanavičy 2	3480	Dolomite	+33.2
Makanavičy 2	3553	Dolomite	+26.0
Makanavičy 2	3553	Dolomite	+28.0
Makanavičy 2	3630	Argillite	+20.9
Malyn 6	3262	Dolomite	+27.0
Malyn 6	3275	Dolomite	+24.7
Malyn 6	3284	Dolomite	+28.4
Navasiolki 1	4438	Limestone	+29.5
Navasiolki 1	4438	Limestone	+31.0
Peršamajsk 21	4633	Dolomite	+28.9
Southern Azemlia 1	3578	Dolomite	+25.3
Vetchin 8	3944	Dolomite	+34.1
Vetchin 8	4074	Dolomite	+20.5
$\bar{x}$ = +27.4 ± 1.0 ‰			

Borehole	Depth of sampling (m)	Host rock	$\delta^{34}S$ (‰)
Famennian (Intersaliferous Formation)			
Biarezina 24	3075	Dolomite	+30.4
Biarezina 24	3273	Dolomite	+30.3
Biarezina 3	1874	Dolomite	+22.1
Biarezina 3	2161	Dolomite	+26.2
Baraviki 2	3634	Dolomite	+29.3
Baraviki 2	3794	Limestone	+32.7
Chalopieničy 1	2314	Dolomite	+29.0
Lojeú 2	1680	Dolomite	+24.9
Navinki 1	3628	Limestone	+36.0
Southern Azemlia 1	3257	Dolomite	+27.9
Žalon’ 2	2483	Dolomite	+28.5
$\bar{x}$ = +28.8 ± 1.1 ‰			

$\bar{x}$ – average value.

Halite occurrence conditions and morphology

Diagenetic halite is abundant in non-evaporite lithofacies of the Prypiac’ Trough. It is common at various stratigraphic levels of the Intersaliferous Formation and of the Subsaliferous Formation including its Devonian and Upper Proterozoic parts (Fig. 4). It was recorded in the upper weathered part of the crystalline basement as well. The halite mineralization is not confined to any specific facies: it is found in deposits of shallow shelf, deep shelf, relatively deep-sea, volcanogenic sedimentary, delta front facies and facies of temporal streams.

Halite is localized in rock under various conditions. Its numerous transparent colorless, more seldom, yellowish crystals, sometimes, rather fine–grained aggregates of white or yellowish–orange color close up cavities, pores, tectonic fissures, stylolitic seams in carbonate and carbonate–clayey rocks (Fig. 5 c, d), form porous and poikilitic cement, infill cleavage cracks in clastic grains of sandstones and gravelites. Sometimes, halite in carbonate rocks is associated with remnants of stenohaline biota, such as corals. In carbonate deposits newly formed halite may be 4 to 6 cm in size, in terrigenous rocks the halite cements comprise 20–30 % of the rock mass.

The post–depositional nature of halite is indicated by extended, sometimes, convexo-concave contacts between quartz grains in sandstones with poikilitic halite cement and by micaceous sheets deformed at contacts with clastic grains. If the halite cement formed first, then it would make the rock consolidation difficult, but a high degree of rock consolidation is evident. Regeneration overgrowths on quartz and feldspar grains enclosed in halite may also serve as evidence of a stage of cement–free rocks in the evolution history of sandstones with halite cement. Sometimes, halite contains oil–bearing inclusions showing the simultaneity of halite formation and hydrocarbon generation and, hence, the diagenetic nature of the mineral.

Halite is more frequently the most recent of the minerals infilling cavities. It usually closes up cavities lined with dolomite and anhydrite crystals and includes the earlier anhydrite plates (Fig. 5d). There are cases when halite and anhydrite formed simultaneously. Mutual relations of diagenetic minerals are representative of a multievent supply of evaporite brines of various chemical compositions into the intersaliferous and subsaliferous deposits and of its complex interaction with these deposits.

Chemical features of halite

The aim of this part of the study was to compare geochemical signals from the depositional halite of the Lower Saliferous and Upper Saliferous Formations and from the diagenetic halite, as well as from the present–day formation brines of the carbonate sediments of the Subsaliferous and Intersaliferous Formations. It was suggested that the diagenetic halite testifies to an intermediate stage of the brine evolution from the environment of evaporative sedimentation to the present–day formation brines.

Ratios of $1{,}000 \cdot Br/Cl$ and $Ca/(Ca+Mg)$ determined for both halite and brine were chosen as geochemical indicators of the brine evolution. There are the following advantages to use these parameters. The pattern of the Br distribution in brine, as well as in the precipitated halite is well-known (Valyashko & Lavrova 1976).

The 1,000 · Br/Cl ratio shows a degree of seawater evaporation.

The components in Ca/(Ca+Mg) are expressed in moles. These values calculated on the basis of the total chemical analysis of halite, on the one hand, and using chemical composition of fluid inclusions in that halite, on the other hand, are almost identical (Table 3). This indicates the predominant occurrence of Ca and Mg in fluid inclusions of halite and gives an opportunity of the direct comparison of the above parameters determined for the solid and liquid phases. The second important attribute of Ca/(Ca+Mg) is that these values calculated for brines vary very slightly in the course of the evaporation process from the beginning of the halite stage to the middle of the sylvite stage (Makhnach & Shimanovich 1991). Thus the Ca/(Ca+Mg) variations in the diagenetic halite are suggested to be signals of Ca and Mg variations in the underground brine during water-rock interaction. To put it more precisely, an increase of Ca/(Ca+Mg) testifies to dolomitization.

The main body of the 1,000 · Br/Cl ratios in the diagenetic halite both in the Subsaliferous and Intersaliferous Formations of the Prypiac' Trough corresponds to the beginning of the halite stage of evaporation (Table 3). At the same time, 7 % of the halite from the Subsaliferous Formation and 20 % of the Intersaliferous Formation halite are characterized by the sylvite stage ratios (0.4–0.6). The 1,000 · Br/Cl ratios of the present–day subsurface brines from the above formations cover the end of the halite stage and the sylvite stage. The comparison of the ratios of halite and formation brine taken from the same intervals shows a wide range of variations for the halite and a narrow range for brine. Moreover, there is a lack of correlation between the values for halite and brine. The above data show that the evaporite brines of the beginning of the halite stage introduced into the Subsaliferous and Intersaliferous Formations from the evaporites played the main part in the diagenetic halite formation. Later on, these brines started being substituted with brines of the sylvite stage. It is very likely that mixing of evaporite brines of gradually increased salinities caused the halite crystallization (Raup 1970).

The Ca/(Ca+Mg) values of the diagenetic halite are significantly higher than those of the depositional halite and significantly lower than those of the present-day formation brine (Table 3). This shows that the main stage of the diagenetic halite formation was accompanied by dolomitization supplied Ca into the underground brine. Afterwards, in the course of input of the new portions of evaporite brines deep into the Subsaliferous and Intersaliferous Formations the dolomitization was going on there.

Thus, the diagenetic halite in non–evaporite lithofacies underlying evaporites can serve as a useful tool to study the water-rock interaction events during the evaporite brine burial. Timing the dolomitization, as well as revealing a succession of the evaporite brine migrations can be carried out by the study of the diagenetic halite chemistry.

DISCUSSION

Almost all investigators who studied mechanisms of diagenetic gypsum, anhydrite and halite formation in subevaporite and interevaporite deposits believe that generation of these minerals was due to the action of brines derived from overlying evaporites. However, no consideration has been given to mechanisms of this interaction. It is important to consider two aspects of this problem: a mechanism governing the evaporite brine supply to the underlying non-evaporite deposits and a mechanism of the diagenetic "evaporite" mineral crystallization in these deposits.

Table 3. Chemical features of halite and brines from evaporite and non-evaporite formations of the Prypiac' Trough.

Lithology, stratigraphy	1000 · Br/Cl				Ca/(Ca+Mg)			
	Halite		Brine		Halite		Brine	
	n	$\bar{x}$	N	$\bar{x}$	n	$\bar{x}$	n	$\bar{x}$
Evaporites, Lower and Upper Saliferous Formations	1425	0.16	*	*	34	0.59	34	0.61**
Carbonates, Intersaliferous and Subsaliferous Formations	26	0.06	347	13.86	26	0.72	347	0.84

n – number of samples studied, $\bar{x}$ – average value.

* no data.

** fluid inclusions in sedimentary halite (after Shajdetskaya 1984).

Mechanism of evaporite brine supply to non–evaporite deposits

Subevaporite and interevaporite zones of sedimentary basins contain sedimentogenic formation brines. These brines derive from surface brines (bittern) that are formed in a halogenesis basin together with evaporite sediments. Sedimentogenic subsurface brines with TDS of 140 to 280 g/l usually occur under regionally consistent gypsum–anhydrite formations, and brines with TDS of 280 to 600 g/l — under evaporite formations composed of rock and potassium–magnesium salts, as well as within and between them.

Two kinds of bittern that form in halogenesis basins in the course of evaporation may be considered: **(a)** above–bottom bittern of the sedimentation zone; **(b)** intercrystal bittern buried in pore space of salt deposits. The bittern of these kinds is supplied into subevaporite and interevaporite deposits in different ways.

The gravity reflux of the above–bottom bittern directly from the sedimentation basin occurs in the process of evaporite accumulation. A possibility of this phenomenon was substantiated experimentally (Polivanova 1977) and by observations in the present–day salt accumulation regions (Kocurko 1979) and at sites of industrial liquid salt waste dumping (e. g., in the Starobin potassium salt deposit in Belarus). A jet penetration of heavy brines into a medium of the lighter subsurface saline water in carbonate and terrigenous deposits underlying an evaporite water basin is aimed at an upward exclusion of the less salted water. This is accompanied by the formation of flowage cones at contacts with poorly permeable blocks and results in the accumulation of the most concentrated brines in the subsurface relief lows.

Above–bottom brines participating in the halogenesis process are abundant. E. g., a body of brines of the sulfate stage of evaporation contained in 4.6 km high column is required to form 20 m thick strata of gypsum.

The accumulation and consolidation of evaporite deposits result some time or other in formation of an impermeable salt or sulfate screen on the way of the above–bottom bittern flowing into the subevaporite strata. In this case the other mechanism of the evaporite brine supply into subevaporite or interevaporite deposits — squeezing of intercrystal bittern — comes into action. The main factor of salt lithification is the creation of skeletal-framework links between salt mineral crystals. This is responsible for large amounts of intercrystal bittern held in rocks at high depths. It may be removed from salt deposits due to their consolidation. There is an essential difference between the intercrystal bittern squeezing and the above-bottom bittern gravity reflux. The first case suggests not only vertical descending movements of brines, but also their lateral migration below halopelitic interlayers both directly along salt beds, and in intrasalt carbonate and sandy members. The lateral migration of the intercrystal bittern in evaporite strata causes the penetration of brine into the older carbonate and terrigenous deposits. The reason is that in many basins the floor of a water body (subevaporite basement) could be topographically dissected already by the beginning of the evaporite sedimentation due to disjunctive tectonics and reef-building processes (Sears & Lucia 1980; Konischev 1984). The bottom relief amplitudes may be as high as several hundreds of meters. In such bathymetrical inhomogeneous water bodies salt sediments are firstly accumulated in the deeper zones; then the salt sedimentation involves the hypsometrical higher levels. Consequently, during the whole time interval when depressions are in filled with salt the conditions are favorable for the lateral squeezing of the intercrystal bittern from the accumulated halogenic deposits to the adjacent blocks of the older subevaporite formations.

Since the subevaporite floor relief amplitudes are high, and salts may be consolidated giving up their intercrystal bittern down to a depth of burial of 250 m and deeper, then the salt accumulation process in evaporite basin lows is accompanied by supply of quite considerable bodies of intercrystal brines to subsaliferous strata. Their amounts can be judged from the following example. A volume of empty space in carbonate and terrigenous rocks of the Intersaliferous Formation of the Prypiac' Trough (200–600 m thick, 25,000 km^2 in area) at present completely in filled with highly salt brines is estimated at 539 km^3. This makes up slightly more than 5 % of the salt volume in the Potassium-Bearing Subformation lying above ($1.03 \cdot 10^4$ km^3). Hence, a 5 % decrease of the salt porosity in the Potassium-Bearing Subformation (it was an order of magnitude higher at sedimentation) accompanied by the intercrystal bittern squeezing made possible infilling the whole intersaliferous reservoir with highly salt brines.

Faults are important paths of the hydraulic communication between horizons and contribute to the brine supply to and redistribution in subevaporite and interevaporite formations. Inside of these formations the redistribution of the brine body and dissolved material is by the gravity transportation and diffusion. Brines of different stages are mixed there with each other and with the initially buried water. These processes are aimed at the replacement of waters inherited from the enclosing rock sedimentation stage by brines and cause diagenetic transformations of non–evaporite rocks in the brine environment (anhydrite, gypsum, halite formation, limestone dolomitization).

The contribution of two mechanisms of the evaporite bittern supply into the subevaporite zones was different in the Prypiac' Trough and in northern and middle Belarus. In the Prypiac' Trough with very thick strata of evaporites formed under conditions of active disjunctive tectonics the intercrystal bittern squeezed played a decisive role in the diagenetic transformation of subsaliferous and intersaliferous rocks. In northern and middle Belarus the process of the bittern gravity reflux from the evaporite sedimentation basin was of primary importance in the diagenetic gypsum formation in subevaporite deposits. A thickness of the Eifelian gypsum strata is too small there (5–20 m) to contain enough intercrystal brine that these could essentially influence the underlying deposits. In addition, calm tectonic conditions and, consequently, a poorly dissected floor of the evaporite basin did not contribute to the migration of intercrystal brines into the subevaporite reservoir.

In closing this part of the paper let's discuss the idea of the nature of solutions that formed the diagenetic anhydrite in Zechstein carbonate deposits of North–Western Europe (Clark 1980). He believes that this mineral formation was due to the action of sulfate solutions derived from dehydration of gypsum beds as a result of their subsiding. We consider this model to be at least not universally true. Let's use this model to the above-mentioned Upper Proterozoic–Lower Devonian deposits of northern and middle Belarus that contain diagenetic gypsum. Let's assume that the bedded gypsum of Eifelian age (maximum 20 m in thickness) occurring in this territory is a product of transformations in a series: gypsum → anhydrite → gypsum. When analyzing the water balance in the first link of this series, it is easy to show that a 20 m high column of absolutely dense gypsum (density is 2.32 t/m^3) when transformed to anhydrite may release a water column barely higher than 9 m. A geochemical effect of this water even fully penetrated in the underlying deposits will be insignificant in a reservoir with thickness of hundreds of meters.

Mechanism of mineral crystallization

Experimental data (Raup 1982) show various possibilities for calcium sulfate precipitation when sedimentogenic brines with the lower (100–270 g/l) and higher (330–430 g/l) salt contents are mixed (Fig. 6). Such mixing repeatedly occurs in subevaporite and interevaporite deposits, when brines of different evaporation degree come there from the overlying evaporite basins and strata. The calcium sulfate crystallization in subevaporite and interevaporite formations may be also due to changes in the chemical composition of brines ($CaCl_2$, NaCl concentrations, etc.) caused by diagenetic transformations of rocks, which results in variations of the sulfate solubility (Zhoglo & Serbin 1980). Besides, the anhydrite and gypsum crystallization is possible when the temperature of brines changes as a result of their penetration deep into the earth and the fluctuations of the heat activity of sedimentary basins in the course of their tectonic evolution.

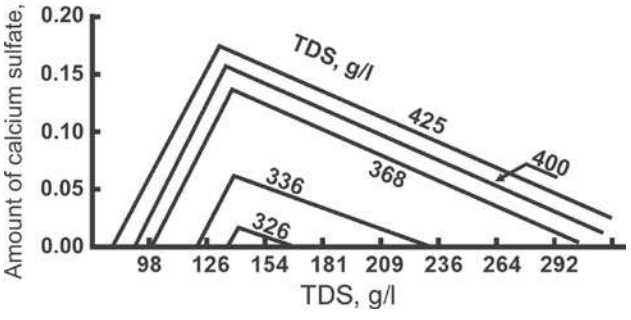

Fig. 6. Amount of calcium sulfate precipitated by mixing 50 ml each of two seawater brines of different total dissolved solids (TDS) at 25° C (after Raup 1982).

Geologically, the mechanism of the diagenetic halite formation in subevaporite and interevaporite complexes is based on the migration of the chloride stage brines saturated or nearly saturated with NaCl to these deposits. This process takes place only in those basins, where chloride salts occur in evaporite strata. The halite crystallization in pores, cavities and fissures of rocks underlying evaporite basins and formations is possible when brines of different evaporation degree supplied there in succession are mixed. The experimental data (Fig. 7) show that the halite is crystallized when brines with a salt content of 400–465 g/l are mixed with those with a salt content of 270–320 g/l (Raup 1970; Zhoglo & Serbin 1981). A physical and chemical explanation of the results of the experiments is an effect of NaCl salting-out with calcium and magnesium chlorides, which is capable to ensure the halite precipitation from brines even not completely saturated with NaCl (Zdanovsky 1972). The water solubility of NaCl decreases by 22 % when the temperature decreases from 200 to 0 C. Ions acting as sodium chloride salting-out agents (e. g., calcium ions) added to a brine cause an increase of the tem-

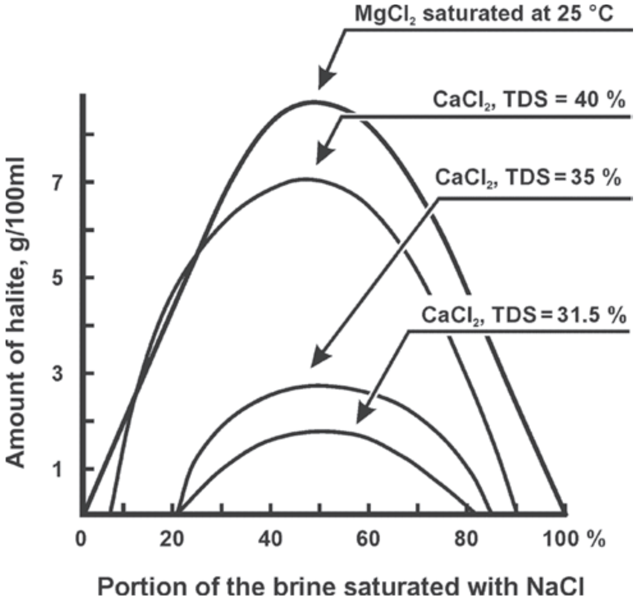

Fig. 7. Amount of halite precipitated from binary mixtures of brines of different compositions and total dissolved solids (TDS) (after Raup 1970 and Zdanovsky 1972).

perature coefficient of salt solubility: when the $CaCl_2$ brine at 20 % concentration is cooled from 100 to 0°C, the NaCl solubility in it decreases by 27 %. There are different geological reasons for the bed temperature decrease that contribute to halite formation: tectonic evolution of basins, ascending movements of brines, etc. A sharp decrease of the reservoir pressure, when tectonic movements take place in fault zones, can be considered as one more factor contributing to the diagenetic halite formation in subsaliferous and intersaliferous deposits.

CONCLUSIONS

Diagenetic gypsum, anhydrite and halite comprise pore, basal, crustification, poikilitic cement of carbonate and terrigenous rocks and are found as nests, nodules, infill fissures, sometimes, substitute the carbonate rock matrix in subevaporite and interevaporite strata.

Diagenetic "evaporite" minerals in subevaporite and interevaporite deposits are typically not confined to any particular formation, stratigraphic unit or facies. These occur in shallow–water and deep–water normal marine deposits, in aqueoglacial and volcanic-sedimentary rocks that are not associated with the evaporating process.

The sulfur isotopic composition of diagenetic sulfate minerals is inherited from the sulfur composition of overlying parent evaporites, but it is slightly heavier due to bacterial sulfate reduction which takes place in the course of the subsurface water–rock interaction. The heavier sulfur isotopic composition of diagenetic sulfate as compared to that of the bedded (sedimentation) sulfate may be used to differentiate them that are not always possible by petrography methods.

A wide range of the $1{,}000 \cdot Br/Cl$ ratio variations for the diagenetic halite testifies to the repeated changing and mixing brines of different salinities within subsaliferous and intersaliferous formations. The Ca/(Ca+Mg) values of the diagenetic halite are significantly higher than those of the depositional halite due to limestone dolomitization which supplies Ca into the underground brine. Thus, the diagenetic halite in a non–evaporite lithofacies underlying evaporites can serve as a useful tool to study the water-rock interaction events during the evaporite brine burial. Timing the dolomitization, as well as revealing a succession of the evaporite brine migrations can be carried out by studying the diagenetic halite chemistry.

The mechanisms of the evaporite brine supply into the carbonate and terrigenous deposits underlying evaporites are the gravity reflux of the above–bottom bittern from a sedimentary basin and the intercrystal bittern squeezing. The first mechanism is characteristic of basins with evaporite strata of small thickness and calm tectonic conditions (e. g., northern and middle Belarus), the second one is common to tectonically active basins with thick evaporite formations and a strongly dissected floor of basins by the beginning of evaporite sedimentation (the Prypiac' Trough).

The crystallization of diagenetic sulfate minerals and halite is due to mixing evaporite brines with different TDS, to brine temperature variations resulted from their penetration deep in the earth and from fluctuations of the heat activity of sedimentary basins in the course of their tectonic evolution, as well as of the reservoir pressure changes caused by tectonic movements in fault zones.

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