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MIOCENE SULFATES OF THE TYRAS'KA FORMATION AT KHODORIV, UKRAINE

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Abstract Geological and mineralogical investigations were performed on sulfates and coexisting minerals from the Badenian Tyras'ka Formation, which is situated near Khodoriv (the Western Ukraine). The following varieties of sulfate rocks were put in evidence: massive, banded, layered, alabaster, veinlet and spotted, saber-like. Gypsum as major mineral as well as anhydrite and calcite as minor phases have been determined using microscopic and X-ray powder diffraction (PXRD) investigations. Microbeam analyses of different types of sulfate-bearing aggregates were performed in order to determine the differences between various generations of gypsum and to establish the order of crystallization. According to these studies, the differences in microstructures related to size and shape of gypsum crystals are: longer and plate crystals in sectors with massive structure, equi-granular within separate layers and spotted sectors, and needles shape in veinlets. In the study area, alabaster is represented by gypsum with high hardness (up to 131 kg/mm^2) and occurs as massive, banded, layered, veinlet, spotted and saber-like. According to investigated relationships between gypsum and other minerals, the order of crystallization is: anhydrite – gypsum – calcite, celestine and quartz.

Keywords*:* Sulfates; Miocene; Badenian; Tyras'ka Formation; Evaporites; Hydrocarbons; Alabaster; Ukraine

1. INTRODUCTION

Sulfate-bearing rocks are a typical component of Miocene sequences of the Western Ukraine. They are widespread in the Pre-Carpathian region (Fig. 1) as a part of the transition zone between the Eastern- and Western-European platforms and the Carpathian foredeep (Kityk et al., 1979). In the transition zone, sulfate-bearing rocks stretch as a belt from the northwest to southeast for about 300 km and range in width from several kilometers up to 40 – 80km. According to Vialov, (1953) and Glushko, (1968) the sulfate-bearing rocks are confined to the Tyras'ka Formation (early known as gypsum-anhydrite suite, or Ckreshatynsky horizon, or Dnistrovskiy horizon for example in Lazarenko et al., 1962; Kudrin, 1966; Sakseev, 1966). The Tyras'ka Formation is of Badenian age, for the definition of the Badenian boundaries, we consider the data set from Gradstein et al., (2012).

Previous works investigated the sulfate-bearing rocks for understanding the regional geological problems as well as ore and hydrocarbons forming processes (Glushko, 1968; Merlich & Datsenko, 1976; Kasprzyk, 1995).

For the sulfate-bearing sequence, the presence of gypsum is related to regional developed evaporitic facies stretching along the Carpathian realm. There are similarities concerning stratigraphical age and succession of facies between the evaporite bearing rocks of the Western Ukraine, Czech Republic, Polish, Moldavian and Romanian Carpathian foredeep basins (Bâgu Gh. & Mocanu Al., 1984; Kasprzyk, 1995; Peryt, 1996; Cehlarov & Ţibuleac, 1997; Cehlarov, 1999; Krzywiec, 2001; Babel, 2004; Peryt, et al., 2004; Poberezhskiy et al., 2002; Peryt et al. 2008, Peryt et al. 2012, Bojar et al., 2018).

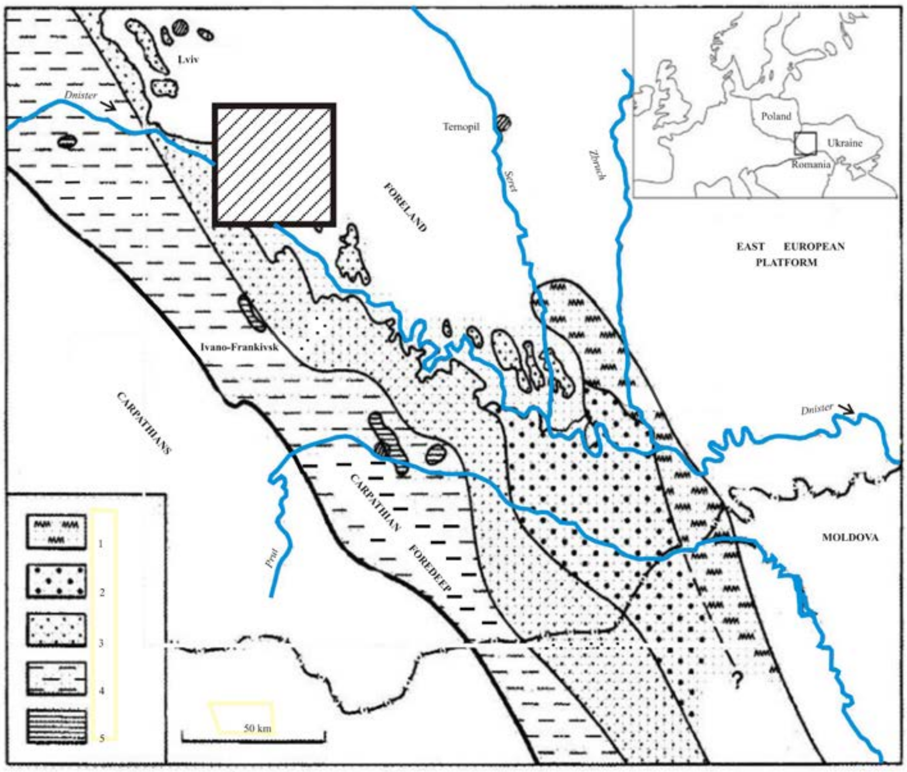

Figure 1. Simplified geological map, modified from Peryt et al., (2004) and Yaremchuk & Poberezhskyi, (2009), showing main tectonic elements of the region as well as the facies zones of the Badenian sulfate rocks, and the studied localities: 1 – facies of stromatolite gypsum; 2– facies of saber and stromatolite gypsum with layers of clastic gypsum; 3– facies of secondary nodular gypsum; 4 – gypsum-anhydrite facies; 5 – salt-bearing areas.

For the investigated region, Badenian sedimentary rocks consist of evaporites as well as deltaic and marine carbonates and siliciclastics. According to Kasprzyk, (1995) and Peryt, (1996), autochthonous and allochthonous gypsum facies were determined and regional correlations for such rocks were proposed.

The primary rocks of the Tyras'ka Formation underwent diagenetic processes (Kasprzyk, 2005), mainly driven by hydrocarbons and bacterial activity (Kubica, 1994) as well as by karstification (Klimchouk, 1996). The products of these transformations have variable texture and mineralogy and are affected also by tectonic activity such as thrust-and-fold deformations connected with movements along faults. As a result, there is a present day hydrocarbon flow (Kachkovskiy & Sckrebta, 1972; Kurapov & Polkunov, 1971) as well as formation of karst and landslides (Gerasimova & Petryshyn, 2010). The most karstified regions are situated to the southeastern end of the zone (Klimchouk, 1996), where famous gypsum caves develop (Optymistychna, Lake Cave, Crystal Cave, etc.). For example, the total length of underground labyrinths of Crystal Cave is around 200 km. Toward the northwestern flank of the zone, karstification is developed sporadically or are even absent.

At the beginning of 19th century the region received commercial interest, fact related to discovery of gas and oil fields in the Carpathian foredeep. Since 1945 the area of the Tyras'ka Formation is under systematic geological investigation and geophysical survey by different exploration organizations as for example "Lvivnaftogazrozvidka", "Ukrnaftogasrozvidka", "Ukrgas", "Ukranaftogeophysics", "Ukrnafta", etc.). As a result, the important role of the sulfate-bearing rocks of the Tyras'ka Formation both as a key reflector and stratigraphic marker for seismic investigations and a regional seal for hydrocarbon in underlying formations was evidentiated. The data are presented for example in the atlas of oil and gas fields of Ukraine, 1998. Additionally, the rocks show evidences of vertical and horizontal hydrocarbons migration (Kachkovskiy & Sckrebta, 1972, Kurapov & Polkunov, 1971).

Beside success in studying the area of the Tyras'ka Formation from the point of view of hydrocarbon exploration, there are a set of problems concerning geology, mineralogy and chemical composition of the rocks and their possible economic significance. For example, the relationship between sulfate-bearing rocks and limestones as main components of the Tyras'ka Formation are not fully understood (Aleksenko, 1961; Parafiniuk, 1989). The role of diagenetic and metasomatic processes for the formation of the rocks and the presence native sulfur deposits is also not yet clear (Merlich & Datsenko, 1976; Kubica, 1994; Kasprzyk, 2005).

A further problem is related to the stratigraphic position of the sulfates rocks in the region. In early works (Gerasimov et al., 2004), the area between Khodoriv up to Dnister River (Fig. 2) was mapped mainly as Cretaceous, even excellent outcrops with gypsum and alabaster of Badenian age are present near Khodoriv and southeastward of Khodoriv (Fig. 2). On the geological map of Gerasimov et al., (2004), Cretaceous rocks are occurring up to the line determined by the villages Novoshino – Kolokolyn – Yavche, where large outcrops with sulfates are located.

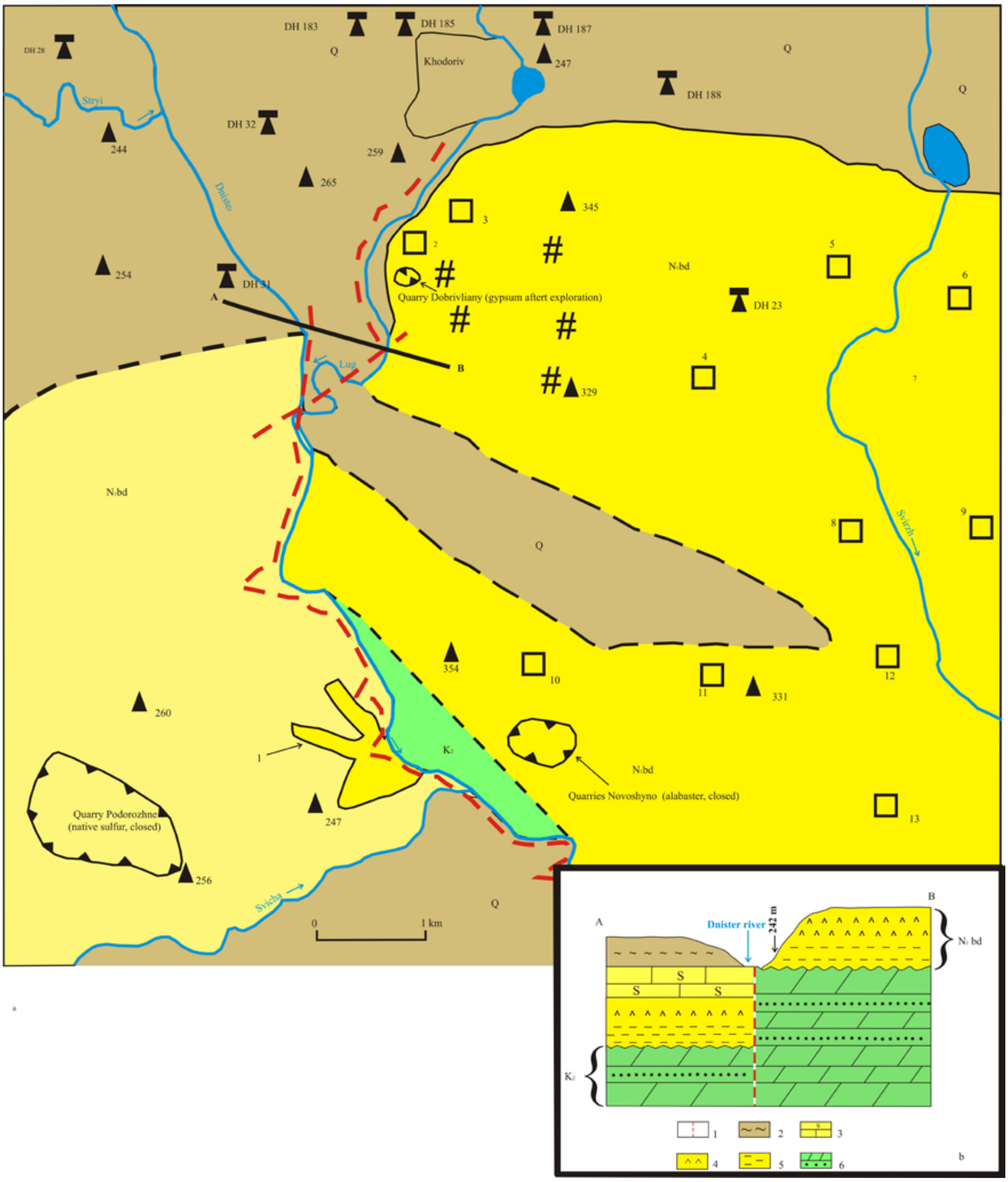

Figure 2. Simplified geological map (a) and idealized geological section (b) of the Badenian sulfate and associated rocks, and the studied localities near Khodoriv. 1 – faults; 2 – Q – Quaternary rocks; 3– the Ratyn limestones with native sulfur; 4 – sulfate bearing rocks; 5 – possible clay horizon; 6 – upper Cretaceous sandstones and marls. Quarries – A – Podorozhne (native sulfure, closed), B – Dobrivliany (gypsum, after exploration), C – Novoshyn (alabaster, closed). Hollow squares - villages, known as places of old stone-cutters and further alabaster quarries: 1 – Zhuravno, 2 – Dobriavliany, 3 – Zagirochko, 4 – Novosiltsi, 5 – Voskresintsi, 6 – Vasyuchyn, 7 – Pidmykhailivtsi, 8 – Zhuriv, 9 – Kolokolyn, 10 – Novoshyn, 11 – Vyshniv, 12 – Cherniv, 13 – Kozary. Triangles – hypsometric points. Triangles with caps – drill holes. Oblique grating – evidences of surface karst.

Mineralogical investigations of the sulfate-bearing rocks were done by Lazarenko et al., (1962) and Kropachova, (1970), but up to now there are no estimations of gypsum – anhydrite quantitative ratios along the investigated section (Bobrovnik, 1962; Koltun & Roskosh, 1969). Additionally, there is no adequate information concerning the development of alabaster within the sulfate-bearing rocks as independent facies as well as its mineralogical characteristics.

Alabaster has been used for various artifacts since thousands of years (Penny, 1993). In Ukraine, alabaster has been utilized for various purposes as for example, building stones for inner decorations or various sculptures (Fig. 3 a - d). In the investigated area alabaster mining date back at least four centuries (Lyubchenko, 1981), for example near Novoshyno, Vasyuchyn, Pidmykhailivtsi, Kolokolyn (see Fig. 2). Alabaster goods (in some places known under the term of "marble" or "Ruthenian marble") can be seen in the Yazvinski's park in Pidnistriany village, Liantskoronski's palace in Rozdil town, Armenian and St. El'zhbet churches in L'viv City (Smirnow, 2005). Buildings and sculptures using this alabaster can be found even in Krakow (Rajchel et al., 2014), Katovice, Zheshuv as well as in various museums and private collections.

Rychlicki (1913) firstly described briefly alabaster occurrences in the region. Later on, data on alabaster distribution in the Tyras´ka Formation was published by Peryt, (1996) and Sliwa, 2009. Specially, the occurrences of alabaster have been described by Dorosh, (2000) and Rajchel et al., (2014). These papers indicate that alabaster was mined from the Zhuravno deposit, located on the right side of the Dnister River. In fact, the Zhuravno village was the former center of alabaster manufacturing of the region, and alabaster was mined from the Novoshyn deposit situated on the left side of the Dnister River. On the Map of Minerals of Ukraine (Thumb-Index, 2001), the Zhuravno deposit is shown as a granite (!) related deposit. Northward of the Novoshyn deposit, occurs the Dobriavliany gypsum deposit with alabaster as well as alabaster outcrops near the Khodoriv town (Fig. 2).

a b c d

Figure 3. Different goods of alabaster: a, – parrot from the studio in Khodoriv; b – model with alabaster of the church in Zhuriv; c – house in the country style with the Zhuravno's alabaster; d – birds.

All the mentioned locations were representing manufacturing sources during the last century. No information is available about alabaster mining before World War I (Kalynets, 1997; Dancewicz, 2003), but according to personal communications, at least three alabaster manufactures had been active in Khodoriv before and shortly after World War II.

Up to now, no data regarding the hardness or mineralogy of the alabaster has been published. Recent mineralogical data for the Egyptian alabaster vessels (Kadera & Mohamed, 2013) indicated also carbonate composition.

According to the above presented problems, detailed investigations of sulphate-bearing sequences of the Pre-Carpathian region by instrumental methods are important from geological and mineralogical points of view as well as from historical and cultural perspective. In this study we present geological, lithological and mineralogical investigations of the sulfates and coexisting minerals from the Tyras’ka Formation of Badenian age, which is situated near Khodoriv (the Western Ukraine), and some conclusions on its peculiarities and origin.

2. SAMPLING AND ANALYTICAL TECHNIQUES

In order to obtain information on the geological position of the sulfate-bearing rocks in the region, we reexamined previous materials available from drillings. Besides, we investigated outcrops from the Tyras’ka Formation near Khodoriv and surrounding areas. Mineralogical investigations including X-ray powder diffraction (PXRD) and microbeam analyses of different morphological-genetic types of sulfates bearing aggregates were performed in order to establish the differences between various generations of gypsum as well as the sequence of crystallization of major and minor phases.

2.1 Samples

Sulfate bearing samples were collected from all morphological varieties of rocks. Description of the investigated rocks are given in Table 1.

2.2 Methods

Mineralogical compositions were determined on whole-rock samples (10 samples) using a BrukerD8 powder diffractometer (PXRD). The samples were prepared and mounted on 1ow background silicon wafers. Taking into consideration the PXRD´s, microbeam analyses were carried out on polished samples using a Jeol JSM-6610 LV scanning electron microscope equipped with Oxford ED- and WD-spectrometers. Analyses included general investigations of sulfate varieties with determination of the composition and relationships of separate phases (25 samples). All these analyses were performed at the Department of Mineralogy, Universalmuseum Joanneum (Graz, Austria).

Hardness of the alabaster was investigated at the Department of Petrography, L’viv National University (L’viv, Ukraine) by direct measurements with a PMT-3 micro indention instrument under a

Table 1. Description and composition of the investigated samples

№	**Description**	**Composition (determined with PXRD)**
1	Rose-yellowish-grey rock with massive structure, coarse-grained, Stinka Hill, Khodoriv	gypsum, anhydrite (minor)
2	Rose-yellowish-grey rock with massive structure, coarse-grained, Dobrivliany deposit	gypsum, calcite, anhydrite, quartz (minor)
3	Light-grey rock with massive structure, fine-grained, Stinka Hill, Khodoriv	gypsum, anhydrite, quartz (minor)
4	White part with massive structure from separate layer of banded sample, Dodrivliany deposit	gypsum
5	White fibrous gypsum (selenite), Stinka Hill, Khodoriv	gypsum
6	White fine-grained sulfate (alabaster), Stinka Hill, Khodoriv	gypsum, anhydrite (minor)
7	White part with massive structure from separate layer of the banded sample, Stinka Hill, Khodoriv	gypsum
8 (etalon) 204	Grey sulfate, Aldan Shield, Seligdar deposit	gypsum, anhydrite, calcite
9 (etalon) 5947-146	White sulfate, Aldan Shield, Seligdar deposit	anhydrite
10 (etalon) 193-826	Light-violet sulfate, Aldan Shield, Seligdar deposit	anhydrite

load of 20g. A diamond pyramid with an angle of 136° has been used for the evaluation of the Vickers hardness. To calculate the obtained data we followed the suggestions of Pudovkina et al., (1966) for different hardness classes. Chemical composition of the spring waters was conducted by classic method of "wet" chemistry at the Regional Branch of GSU KP "Kirovgeologia" (Kyiv, Ukraine).

3. GEOLOGICAL FRAMEWORK OF THE AREA

The Tyras'ka Formation overlies different older formations of Miocene and Cretaceous age (Dolenko, 1962). Glushko, (1968) reports an increase of terrigenous input and salt accumulations towards the Carpathians, in some places salt-bearing clays being a major component. An important factor of the Tyras'ka Formation structure is driven by an old relief, which was formed as the result of erosion before the Badenian times (Atlas of oil and gas fields of Ukraine, 1998). This relief is represented by valleys, the most significant being the Khodoriv and Kolomiya valleys (Atlas of oil and gas fields of Ukraine, 1998; Gozhyk et al. 2013). Badenian sediments overlap the old relief and form anticlinals and synclinals over benches and valleys. The geological frame around the town of Khodoriv and along Dnister, Stryi and Lug Rivers is complicated by the presence of faults along which blocks are displaced horizontally or vertically up to 100 m, forming uplifted blocks and depressions (Gerasimova & Petryshyn, 2010) (Fig. 2).

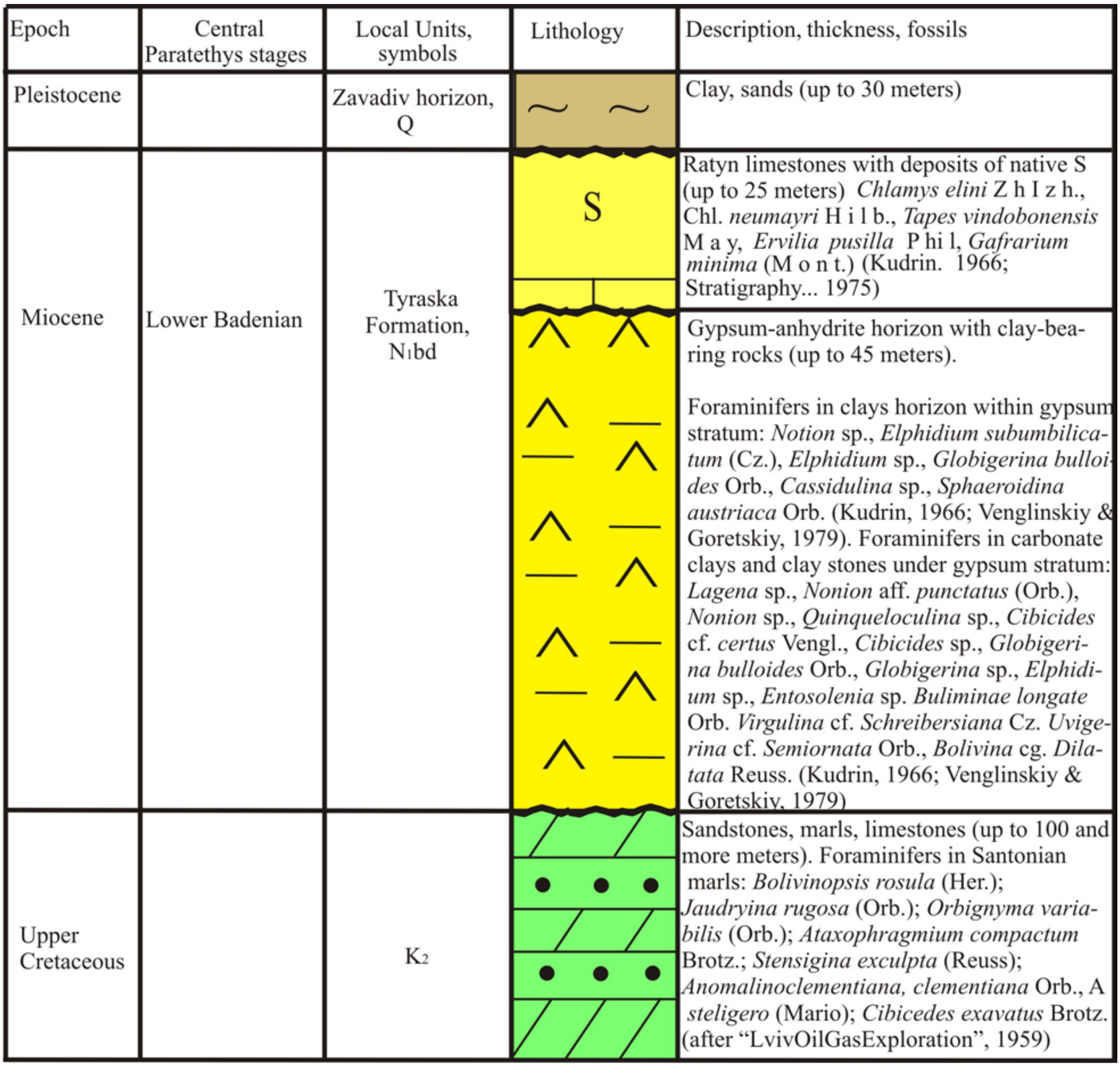

Figure 4. Stratigraphic column generalized for the area, including biostratigraphy with foraminifers' zonation. After Sakseev, (1966); Venglinskiy & Goretskiy, (1966); Glushko, (1968); Gozhyk et al., (2013).

Evaporites of the Tyras'ka Formation are deposited above the Lower Badenian consisting from top to bottom of carbonates, tuff-sandstones and bentonites (Vialov, 1953; Glushko, 1968). The data from the exploration drilling for native sulfur deposits indicate that the Ratyn Limestone of Upper Badenian age overlies the sulfates rocks of the Tyras'ka Formation (Sakseev, 1966) (Fig. 4). The Ratyn Limestones occurs only in the western part of studied area (see Fig. 2). Some authors (Sakseev, 1966; Venglinskiy & Goretskiy, 1966) mention the replacement of the sulfate-bearing rocks of the Tyras'ka Formation by the Ratyn Limestones. Small size lenses of limestones, clays, increasing amount of terrigenous materials as well as salt within the sulfates-bearing strata were described. In some parts of the Tyra'ska Formation natural sulfur of industrial importance occurs in the younger horizons of the Ratyn Limestone.

Investigation of drill materials from the north and north-west of Khodoriv (see Fig. 2) indicated Cretaceous marls and sandstones underlying the Tyras'ka Formation (DH-178, DH- 183, DH-23, etc. In marls (DH-183), Cretaceous (Santonian) forms of foraminifers were determined (see Fig. 4).

Nannofossils from clays within and below the gypsum (Kudrin, 1966; Venglinskiy & Goretskiy, 1979) indicate the presence of the NN5 and the lower part of the NN6 calcareous nannofossils zones (Martini, 1971; Bondarchuk et al. 1975; Gozhyk et al. 2013). Foraminifera from the Tyras'ka Formation indicate the M6 and M7 planktonic formainifera zones, thus a similar stratigraphic position (Bergren et al., 1995).

On the right side of the Dnister River, the Podorozhnens'ke sulfur deposit (at present closed) is located. The drilling cores indicate that sulfur is mainly connected with the Ratyns'k limestones, only minor amount of native sulfur being situated in the stratigraphically older sulfate-bearing horizons. All major morphological varieties of the Tyras'ka sulfate-bearing rocks, including alabaster, were put in evidence in the drill cores. Rocks of the Podorozhnens'ka structure are situated hypsometrically below the Tyras'ka sulfate-bearing rocks on the left side of the Dnister River, a fault being present along the river (Fig. 2). For the Ratyn Limestones (Fig. 4) the following macro-fossils were described: *Ervillia* cf. *pusilla* Phil., *Venus* ef. *marginata* Hoern, *V.* sp., *Isocardia* sp., Ostrea *digitalina* Dub., Ostrea sp., *Pecten gloriamaris* Dub., *Trochus guadristriatus* Dub., *Tapes* sp., *Chlamys neumayri* Hilb., *Pecten* sp., *Cardium* sp. et al., (Dolenko, 1962), indicating marine environment.

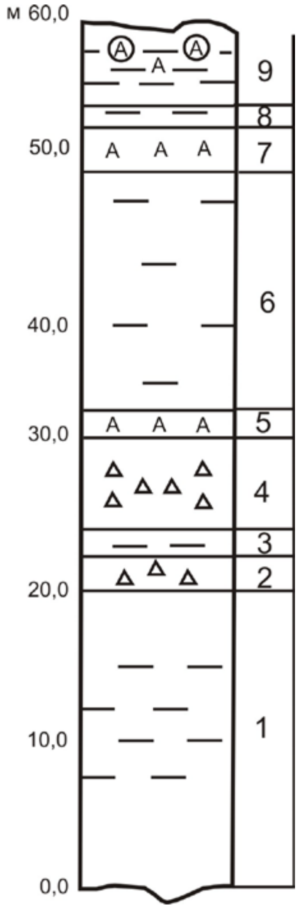

Figure 5 Geological section of the sulfate-bearing rocks of the Tyras'ka Formayion at the left bank of the Lug River southward of Khodoriv town. Legend: 1, 3, 6, 8 – massive light-grey gypsum and layers and lenses of small-grained plate gypsum; 2, 4 - stratified coarse and medium grained gypsum rich in clays, and blasted; 5, 7 - alabaster inclusions and separate layers of white fine grained alabaster; 9 – intercalation of massive and banded gypsum and fine grained alabaster with alabaster boulders.

4. RESULT AND DISCUSSIONS

4.1 Composition and structure of the sulfate sequence of the Tyras´ka Formation

Sulfate-bearing outcrops of the Tyras'ka Formation are situated on the Stinka hill, on the left bank of the Lug River southward of the Khodoriv town (Fig. 2). In figure 5, from bottom to top several facies were put in evidence and simplified lithological column is given for the Stinka hill area. Massive light – grey gypsum (# 1) is situated at the hypsometric level of 318m. Massive light-grey gypsum (Fig. 6) and layers and lenses of small-grained plate gypsum (from # 1 up to # 2, and similar to # 6, 8) have a total thickness about 20m.Large and elongated crystals of gypsum are grown within the layered gypsum (up to # 2). The next interval (with a thickness about 5m) is represented by relative massive grey gypsum with sporadically large crystals. From the massive gypsum (# 1) up to the alabaster layer (# 5) there is stratified coarse to medium grained gypsum rich in clays (Fig. 6c), the thickness of this interval being about 8m. Alabaster inclusions (up to few centimeters) appear near the top of the interval, and then (# 7) separate layers of white fine grained alabaster (thickness up to 1m) are intercalated with layers of massive grey and yellow gypsum (Fig. 6d).

Near the top of Stinka hill (# 9, hypsometric level of 348m) there are a series of outcrops with grey-yellow massive gypsum and banded grey gypsum and white fine grained alabaster (thickness up to several centimeters).

Figure 6. Typical sulfate-bearing rocks from outcrops within observed area. a – massive and banded structures in outcrops near Khodoriv; b – large and elongated gypsum crystals concentrated into separate layers in coarse-grained gypsum rock. 1.2 km to the east from Pidmykhailivtsi village; c – coarse-grained gypsum rock rich in clays; d – intercalation of alabaster layer and coarse-grained gypsum rock; e – banded gypsum and alabaster with white alabaster ball; f – banded structures of gypsum with fibrous veinlet of gypsum, Stinka Hill near Khodoriv; g – fragments of gigantic gypsum crystals in coarse grained laminated matrix, 1.5km to the east from Pidmykhailivtsi village; h – alabaster layer near Vilkhova village.

White alabaster boulders (from few centimeters up to 1.5m in diameter) are developed close to the top of hill (hypsometric level of 351m) within layered or relatively massive grey and yellow gypsum (Fig. 6e). In some separate outcrops, near the top, layers of fibrous gypsum (thickness from few centimeters up to 0.1m) are developed (Fig. 6f). Sometimes the fibrous gypsum is discontinuous and bent.

Massive and layered gypsum are the main components of the sulfates sequence near Khodoriv, alabaster and fibrous gypsum are minor varieties. Alabaster is developed mainly in the upper part of the sequence and boulders of white alabaster are located near the top of the sequence. The upper part of the Stinka hill presents surface karstification. Similar forms can be found several kilometers from the south-east to the south-west of the Stinka hill (see Fig. 2 a). The total preserved thickness of the sulfate-bearing sequence of the Stinka hill is up to 35m.

Laterally we found similar varieties of gypsums (see Fig. 2 a), but with variable proportions of the already described types. The area of alabaster expands to south and south-west up to Dobrivlians'ke gypsum deposit (distance is about 4 km) and to the Novoshyno gypsum deposit (distance is about 15km) (see Fig. 2 a). The last deposit is located on the top of a hill named Bakotsyn near Novoshino village on the left bank of the Dnister River. At Bakotsyn, alabaster has been quarried for centuries. The second old alabaster manufacturing center is Bowshiv, (outside the area, Fig. 2), and the third historically famous alabaster place is near Kolokolyn village (Fig. 2). Alabaster from these localities has been found as layers and elongated lenses with up to few meters thick. It is characterized by homogenous white color, but some varieties colors (from yellow and grey to black) are known as well. The alabaster forms thin (up to few millimeters) to thick (up to few dozen centimeters) layers or nests, and only sometimes it forms thick (up to few meters) layers. During present investigations, we found massive alabaster with a similar quality (Fig. 6h) near the Vilkhova village northward of villages Zhuriv and Kolokolyn (Fig. 2). At the same time, in the Boyim Chapel (1606-15) in L'viv City there are sculptures made in honeyed massive alabaster from the Bakotsyn hill, but this type cannot be anymore found.

Besides these varieties of gypsum another morphological type was locally determined. Thin layered (Fig. 6f) gypsum is developed in several outcrops eastward of the Pidmykhailivtsi village. This type of gypsum is similar laminated as the gypsum described by Peryt et al., 2008 at the easternmost part of the Badenian rocks from the Western Ukraine. In the outcrops near Pidmykhailivtsi village we observed also large and elongated crystals (up to several centimeters) of light yellow up to pale blue gypsum, which is concentrated into separate layers (Fig. 6b). In the same outcrops we detected fragments of large gypsum crystals in more fine grained cements (Fig. 6f). Saber-like gypsum develops also sporadically and it is represented by large and elongated light-yellow crystals (up to several centimeters), similar to saber gypsum from the famous gypsum caves of the Tyras'ka Formation (Klimchouk, 1996, 1997). Wider and longer gypsum crystals the same size as the former, transparent or grey in color were found in separated layers and nests, showing no preferred crystal orientations. Larger (up to dozens of centimeters) yellow and reddish-yellow crystals of gypsum are typical for saber-like varieties.

Massive gypsum is developed mainly in the lower part of the sections, and fibrous gypsum is concentrated in the upper part of the sequences.

4.2 Hydrocarbon bearing strata

Rocks of the Tyras'ka Formation, with a thickness of up to 60 m are a reliable marker for the external zone of the Carpathian foredeep (Glushko, 1968) containing hydrocarbon accumulations (Atlas of oil and gas fields of Ukraine, 1998). The sulfate-bearing rocks of the Tyras'ka Formation is a key reflector for seismic investigations and the adjacent younger clay-sandy Kosiv Formation (to 1200m) is a regional seal for hydrocarbons of the underlying formations (Atlas of oil and gas fields of Ukraine, 1998). Some small scale (less than 1 billion cubic meters) gas fields (Krekhiv and Sykhiv fields) were recently discovered at the south western corner of the Tyras'ka Formation area (see Fig. 2).

Near to the native sulfur deposits permanent flows of hydrocarbon gases were detected (Merlich & Datsenko, 1976), and weak methane emanations occur. Deep hydrocarbons flows are considered responsible for the origin of the native sulfur deposits related to transformation of sulfates of the Tyras'ka Formation (Kurapov & Polkunov, 1971; Kachkovskiy & Sckrebta, 1972). Sulfates are rich in solid, liquid and gases hydrocarbon inclusions similarly to other famous evaporite sediments at Sicilia, Near Caspian areas, Bosnia, etc. (Sonnenfeld, 1984). Concentrations of the organic matter typically vary from 0.02 % up to 0.06% (Zelizna & Filts, 1971). Such low levels of organic matter do not generate hydrocarbon deposits therefore, a mechanism of vertical hydrocarbons migration is proposed (Kurapov & Polkunov, 1971; Kachkovskiy & Sckrebta, 1972) in order to explain gas, oil and sulfur deposits as well as zonal distribution in connection to faults.

During present investigations near Khodoriv we found on the water surface of a spring near Lug River drops of hydrocarbons. The lower level of the outcrops near Khodoriv is just above the Lug River, so these rocks may contain hydrocarbons.

The spring has a total mineralization of up to 45647.9 mg/l (Table 2) with Na^+, Cl^-, and SO_4^{2-} as main ions. Between this spring and the mineral waters of 'Naftusia' type developed in similar sulfate-bearing rocks there is a large difference (Table 2). According to gas chromatographic investigations there are only trace methane concentrations in the spring water. The mineralized spring can be an indicator of older sulfate-bearing strata than the sulfate-bearing sequence of the Tyras'ka Formation as documented for other locations of the Pre-Carpathian region (Glushko, 1968). The sulfate-bearing rocks are impermeable covers favorable for hydrocarbon accumulation, but related to different fault systems large scale hydrocarbons flow is possible. At the same time, ground-water from different levels of the geological sections have individual compositions (Table 2).

4.3 Mineralogy

The main mineral of the rocks with massive texture is grey and rose-grey coarse-grained gypsum. Intercalations of white and rose-grey fine-grained gypsum form layered and banded varieties. Gypsum is a major mineral (up to 97 - 99% of total volume of the rock) in all types of sulfate-bearing rocks in this region. Anhydrite, calcite, celestine and quartz are minor phases. Al-hydroxides along with some undetermined phases are sporadically present in the rose-yellowish-grey rocks with massive texture (Fig. 7a). Chemical analyses indicate beside high Al content, small contents of Ca and S, which are most probably related to gypsum matrix and a low analytical sum (Al_2O_3 – 70.53; SO_3 – 1.09; CaO – 1.10, weight %,). Due to analytical problems (small grain size and rough surface) it was not possible to obtain better analyses and distinguish between natural Al-hydroxides $Al(OH)_3$ and AlO(OH) groups. The presence of Al-hydrates explains partly yellow and rose color of the massive sulfate rocks.

In the massive, layered and banded varieties, gypsum occurs in form of elongated plates (up to 35μm in length) with sub-parallel orientations. It composes almost mono-mineralic layers and sectors, with rare single elongated grains (up to 45μm in length) of anhydrite relics (Fig. 7b) or late formed crystals (up to 40μm in length) of quartz, calcite and celestine (Fig. 7c). Sometimes calcite and celestine crystals form aggregates, which fill fractures or inter-crystalline spaces between gypsum grains (Fig. 7d, e), in these case being obviously younger as gypsum.

Table 3. Data on direct measuring of hardness of the alabaster (sample № 6)

N	Hardness in kg/mm2	Note
Average	77.54	Data are homogenous
Limits	58 – 103	

Note. For calculation of measured data we used the method of Pudovkina et al., 1966.

Table 2 Chemical composition of waters from different sources

Components (g/dm^3)	**Spring near Khodoriv**	**DH-178/475 limestone**	**Mineral water 'Naftusia' type from Truskavets region***	**Mineral water 'Naftusia' type from Podil region***
Na^+	14858.0	341.19**	4.51 – 6.7**	125.5 – 134.4**
Ca^{2+}	1523.0	325.85	75.4 – 130.0	52.1 – 60.6
Mg^{2+}	619.7	193.22	43.7 – 88.15	36.5 – 42.6
Sum cations	17000.7	860.26	41.2 – 74.95	214.1 –237.6
CO_3^{2-}	3.0	-	-	-
HCO_3^-	366.1	244.08	381.4 – 509.4	427.3 - 475.9
Cl^-	24250.1	31.91	22.7 – 53.2	67.4 – 84.0
SO_4^{2-}	4031.0	2053.8	53.8 – 65.0	82.3 – 96.4
NO_3^-	0.1	-	0.1 – 2.2	-
Sum anions	28647.2	2329.8	114.5 – 157.4	577.0 – 656.3
Total sum	45647.9	3190.05	153.7 – 232.35	791.1 - 893.9
Dry rest 105ºC	26096	244	-	-
pH	6.8	6.5	7.2 – 7.9	7.4 – 7.56

*After (Shestopalov et al., 2009) ** $Na^+ + K^+$

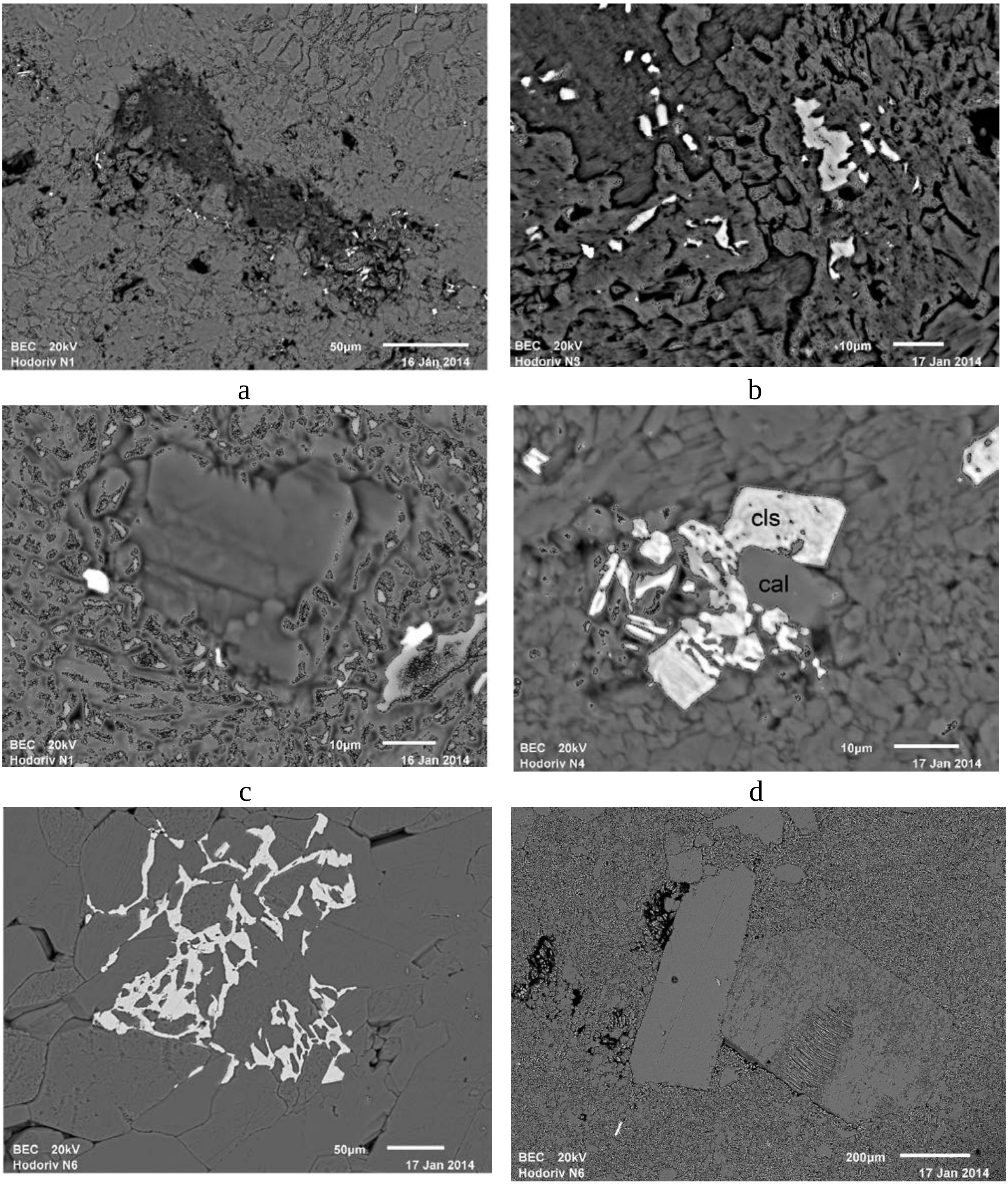

Figure 7 Scanning electron microscope image, BSE mode. a - Al-hydroxides in gypsum; b - gypsum crystals with anhydrite relics in middle grained sulfate rocks; c - authigenic quartz in gypsum aggregates; d - coexisting crystals of calcite (cal) and celestine (cls) in gypsum aggregates; e - intergranular celestine in gypsum matrix; f - large gypsum crystals in relative equigranular masses of fine grained alabaster.

Fine grained alabaster is represented by relatively isomorphic grains of gypsum (up to 10µm) (Fig. 7f). Distinct large and long single crystals of gypsum (up to 600µm) are developed in a relatively equigranular mass of fine grained gypsum. Alabaster has a higher hardness (up to 103 kg/mm^2, Table 3), which is the most important difference between alabaster and other kinds of gypsum in the region. Obtained data on hardness of the alabaster (Table 3) are in limits of gypsum and anhydrite hardness reported before (Lazarenko et al., 1962) for sulfates from other places of the gypsum-anhydrite horizon. Besides it, there is no further structural difference between the alabaster and massive gypsum from the sulfate-bearing rocks near Khodoriv and surrounding territory.

In all morphological varieties of the sulfate-bearing rocks, gypsum has relatively stable chemical compositions and it does not contain any important trace elements (Table 4). We found similar peculiarities for chemical compositions of anhydrite (Table 5). In both Mg, Sr and Ba are below the detection limits. Late authigenic calcite has occasionally higher content of Mg, Sr, S, Mn, Na (Table 6-7). Mg, Sr, Mn are incorporated in the calcite structure, the presence of the other elements can be explained by matrix effects.

Table 4 Chemical composition of gypsum from area of Khodoriv

Sample	N1	N1	N3M	N3M	N6C	N6C	N6M	N6M	N6Ma	N6Ma	N6F	N6F	N7M	N7M
Element	1	2	1	2	1	2	1	2	1	2	1	2	1	2
SO_3	53.15	1.00	54.34	0.99	56.61	1.00	56.91	1.00	56.71	1.00	45.88	1.00	46.71	1.00
CaO	37.94	1.01	39.42	1.03	40.13	1.01	39.75	1.00	39.94	1.00	32.48	1.01	33.08	1.01
Cationsum		2.01		2.02		2.01		2.00		2.00		2.01		2.01

1 - Weight %; 2 – Number of ions; C – Crystal; M – Matrix, F- Frame

Table 5 Chemical composition of anhydrite relics in gypsum from area of Khodoriv

Sample	N1	N1	N3a		N3a	N3b	N3b	N3C	N3C	N4C	N4C	N6	N6	N7a	N7a	N7b	N7b
Element	1	2	1		2	1	2	1	2	1	2	1	2	1	2	1	2
SO_3	57.53	1.00	59.02		1.00	54.98	1.00	59.45	1.00	59.33	1.00	59.32	1.00	59.47	1.00	58.08	1.00
CaO	39.76	0.99	41.32		1.00	38.10	0.99	41.75	1.00	41.86	1.01	41.55	1.00	41.53	1.00	40.52	1.00
Cation Sum		1.99			2.00		1.99		2.00		2.00		2.00		2.00		2.00

1 - Weight %; 2 – Number of ionson the basis of 4 oxygen atoms; C – Crystal; M – MatrixFrame

Table 6 Chemical composition of authigenic calcite in gypsum from area of Khodoriv

Sample	N1	N1	N1	N1	N1	N1	N1	N1	N3	N3	N4	N4	N4	N4
Element	1	2	1	2	1	2	1	2	1	2	1	2	1	2
CaO	51.77	0.95	51.42	0.92	51.55	0.94	52.27	0.94	51.93	0.94	52.69	0.92	53.59	0.90
MgO	-	-	1.18	0.03	-	-	0.52	0.01	-	-	1.13	0.03	1.72	0.04
SrO	1.66	0.02	-	-	1.04	0.01	-	-	-	-	-	-	-	-
SO_3	0.82	0.01	1.44	0.02	1.01	0.01	1.26	0.02	1.45	0.02	1.36	0.02	1.14	0.01
MnO	-	-	-	-	-	-	-	-	-	-	0.42	0.01	1.86	0.02
Na_2O	-	-	-	-	0.41	0.01	-	-	-	-	-	-	-	-
Cation sum		0.98		0.96		0.98		0.97		0.96		0.97		0.97

1 - Weight %; 2 – Number of ions on the basis of 1 oxygen atom

Table 7 (continuation) Chemical composition of authigenic calcite in gypsum from area of Khodoriv

Sample	N7a	N7a	N7b	N7b	N7c	N7c	N7d	N7d
Element	1	2	1	2	1	2	1	2
CaO	52.17	0.95	51.65	0.95	50.65	0.91	51.61	0.94
MgO	0.58	0.01	0.57	0.01	0.94	0.02	0.65	0.02
SrO	-	-	-	-	1.51	0.01	-	-
SO_3	0.89	0.01	0.91	0.01	1.37	0.02	0.98	0.01
MnO	0.27	0.00	0.21	0.00-	0.35	0.00	0.76	0.01
Cationsum		0.98		0.98		0.97		0.98

1 - Weight %; 2 – Number of ions on the basis of 1 oxygen atom

Table 8 Chemical composition of idiomorphic authigenic celestine in gypsum aggregates from area of Khodoriv

Sample	N1	N1	N1	N1	N4	N4	N6K	N6K	N6C	N6C	N7	N7
Element	1	2	1	2	1	2	1	2	1	2	1	2
SO_3	44.31	1.01	45.52	1.01	44.90	0.99	43.69	1.00	43.11	1.00	43.63	1.00
SrO	55.33	0.97	56.19	0.96	58.20	1.00	55.55	0.98	54.52	0.98	55.20	0.98
BaO	0.21	-	0.86	0.01	0.94	0.01	-	-	-	-	-	-
CaO	0.37	0.01	0.49	0.02	0.25	0.01	0.44	0.01	0.52	0.02	0.48	0.02
Cation sum		1.99		1.99		2.01		2.00		2.00		2.00

1 - Weight %; 2 – Number of ions on the basis of 4 oxygen atoms

Table 9 Chemical composition of celestine rich in Ba in gypsum from area of Khodoriv

Sample	N7a	N7a	N7b	N7b
Element	1	2	1	2
SO_3	43.12	1.00	40.35	1.00
SrO	46.33	0.83	40.00	0.77
BaO	12.37	0.15	17.56	0.23
CaO	0.16	0.01	0.26	0.01
Cation sum		1.99		2.00

1 - Weight %; 2 – Number of ions on the basis of 4 oxygen atoms

Late grown crystals of celestine have higher Ba-contents (Table 8, 9). Reverse ratios between amounts of Sr and Ba ($Sr_{0.83}Ba_{0.15}Ca_{0.01}S_{1.00}$; and $Sr_{0.77}Ba_{0.23}Ca_{0.01}S_{1.00}$) indicate a solid solution.

5. CONCLUSIONS

Sulfate-bearing rocks are main components of the Tyras'ka Formation of Badenian age, present in numerous outcrops near Khodoriv. The geological frame around the town and along Dnister, Stryi and Lug Rivers is complicated by the presence of faults along which blocks are displaced horizontally or vertically up to 100 m, so younger strata of the Ratyn Limestones of Upper Badenian age are present only in some depressions. Besides, different older formations of Miocene and Cretaceous age can be found in uplifted blocks cut by rivers.

Geological and structural evidences as well as direct hydrocarbons flows in mineral waters near Khodoriv and some small gas fields support the idea concerning the importance of the Tyras'ka Formation for the oil and gas industry not only within the well-known districts but also for the new areas.

The sediments were formed in a marine environment, and the different morphological types of the rocks are reflecting distinct facies. Massive, banded layered, saber-like, alabaster, veinlet and spotted morphological and compositional varieties of the sulfate rocks were put in evidence. Massive gypsum is developed mainly in the lower part of the sections, fibrous gypsum in the upper part of the sequences.

Within the investigated area the main sulfate mineral of the Tyras'ka Formation is gypsum, the minor phases being represented by anhydrite, calcite, celestine and quartz. Anhydrite and quartz have relict nature. Minor authigenic minerals containing Sr and Si are present.

The differences in microstructures of the rocks are related to variation in sizes and shapes of gypsum crystals: longer and plate crystals in sectors with massive structure, more equi-granular within separate layers and spotted sectors, and needles shape in veinlets. In the study area, alabaster is represented by gypsum with high hardness (up to 131 kg/mm^2) and occurs in sectors with fine grained isometric structures. Alabaster from these localities has been found as layers and elongated lenses with common thickness up to few meters. Occurrence of alabaster shows regional development and can be a good frame for the development of mining in this region for different purposes.

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