

CLAY MINERALS OF MIOCENE EVAPORITES OF THE CARPATHIAN REGION, UKRAINE

MINERAŁY ILASTE W EWAPORATACH MIOCEŃSKICH REGIONU KARPACKIEGO, UKRAINA

PETRO BILONIZHKA¹, IAROSLAVA IAREMCHUK², SOPHIYA HRYNIV², SERHIY VOVNYUK²

Abstract. Based on previously published XRD and DTA-TG data, the clay mineral assemblages composition of water-insoluble residue of Miocene evaporites of the Ukrainian Carpathian region is presented. Data on the composition of pelitic fraction minerals were obtained from studies of Egerian–Eggenburgian and Badenian evaporites of the Carpathian Foredeep, namely gypsum, rock salt and potash salts of the Stebnyk and Kalush-Holyn’ deposits, and rock salt from the Transcarpathian Trough. In the gypsum facies, the clay minerals are mainly allogenic and are represented by dioctahedral smectite, illite and chlorite, while authigenic minerals such as trioctahedral smectite and illite are present in minor amounts. Clay minerals of rock salt facies are represented by illite, chlorite and mixed-layer illite-smectite in Egerian–Eggenburgian rock salt. In Badenian rock salt, smectite, corrensite and mixed-layer chlorite-smectite are also present. In potash facies deposits, only illite and chlorite occur. The degree of transformation of clay minerals depends upon basin brine concentration. As the brine concentration increases, the mineral assemblage changes towards vanishing of swelling clay minerals. Volcanic activity had also a great impact on clay minerals composition – pyroclastic material alteration resulted in the occurrence of smectite, corrensite and mixed-layer chlorite-smectite in the Badenian rock salt.

Key words: clay minerals, Miocene evaporites, Carpathian Foredeep, Transcarpathian Trough, Ukraine.

Abstrakt. Skład asocjacji minerałów ilastych ewaporatów mioceńskich karpackiego regionu Ukrainy podsumowano na podstawie opublikowanych wyników badań dyfraktometrycznych i termicznych ewaporatów egeru–eggenburgu i badenu zapadliska przedkarpackiego, a mianowicie gipsu, soli kamiennej i soli potasowej z Stebnyka i Kałuszu, a także badeńskiej soli kamiennej z Sołotwyna i Mukaczewa (Zakarpacie). W ewaporatach facji gipsowej dominują alogeniczne minerały ilaste (smektyt dyoktaedrychny, chloryt i illit), a autigeniczne minerały (smektyt tryoktaedrychny, illit oraz minerały mieszanopakietowe) są obecne w małych ilościach. Minerały ilaste facji soli kamiennej egeru–eggenburgu zawierają illit, chloryt i mieszanopakietowy illit-smektyt, a w soli kamiennej badenu, oprócz tych minerałów, obecne są jeszcze smektyt, korensyt oraz minerał mieszanopakietowy chloryt-smektyt. W solach potasowych z minerałów ilastych występują tylko illit i chloryt. Stopień transformacji minerałów ilastych w ewaporatach regionu karpackiego zależy od stężenia solanek basenu ewaporatowego w czasie ich depozycji. Wraz ze wzrostem koncentracji solanek asocjacje minerałów ilastych zmieniają się w kierunku zmniejszenia ilości smektytu i mieszanopakietowych faz i uporządkowania ich struktury. Istotny wpływ na skład minerałów ilastych ma aktywność wulkaniczna – materiał piroklastyczny zamienia się w smektyt, korensyt i mieszanopakietowy chloryt-smektyt, które występują w badeńskiej soli kamiennej.

Słowa kluczowe: minerały ilaste, ewaporaty miocenu, zapadlisko przedkarpackie, zapadlisko zakarpackie, Ukraina.

¹ The Ivan Franko National University of Lviv, Ukraine, Hrushevskyy 4, 79005 Lviv, Ukraine

² Institute of Geology and Geochemistry of Combustible Minerals of NAS of Ukraine, Naukova 3a, 79060 Lviv, Ukraine; e-mail: sophia_hryniv@ukr.net

INTRODUCTION

Clay minerals are indicators of conditions of rock formation and alteration during early and late diagenesis; to a considerable extent it concerns evaporite rocks as well. In the Carpathian region of Ukraine, evaporites belong to several stratigraphic levels and are represented by deposits of different facies – gypsum, anhydrite, and rock and potash salts.

Mineral composition of clays of the evaporites from the Carpathian region is quite well studied (Tab. 1). In the Ukrai-

nian Carpathian Foredeep, the clay mineral composition of potash salts facies consists of illite and chlorite (Yarzhemskaya, 1954; Bilonizhka *et al.*, 1966; Ivanov *et al.*, 1980; Hryniv *et al.*, 1993; Oliyovych *et al.*, 2004). The clay mineral assemblage of halite facies consists of illite, chlorite, mixed-layer minerals and rarely smectite in the Carpathian Foredeep (Iaremchuk, Hryniv, 2008; Iaremchuk, Galamay, 2009) and illite, chlorite (Bilonizhka, 1979) and mixed-layer chlorite-smectite and corrensite (Kityk *et al.*, 1983; Gabinet,

Table 1

Minerals of pelitic fraction of water-insoluble residue from Miocene evaporites of the Carpathian region, Ukraine

Facies	Age, suite	Number of samples	Generalized mineral composition of pelitic fraction of water-insoluble residue							Source	
			Clay minerals						Other minerals		
			It	Ch	Sm	Co*	Ch-Sm	It-Sm			
Potash salts	Badenian, Tyras (Kalush–Holyn' deposit)	6	++	+	–	–	–	–	–	Yarzhemskaya (1954)	
		8	++	++	–	–	–	–	Mg, (Ca)	Bilonizhka <i>et al.</i> (1966)	
		25	++	++	–	–	–	–	Mg	Oliyovych <i>et al.</i> (2004)	
	Vorotyshcha suite, Eger–Eggenburgian (Stebnyk deposit)	8	++	(+)	–	–	–	–	Mg, (Do)	Yarzhemskaya (1954)	
		6	++	++	–	–	–	–	Mg, (Ca)	Bilonizhka <i>et al.</i> (1966)	
		–	++	++	–	–	–	–	Q, Mg, Do	Ivanov <i>et al.</i> (1980)	
		7	++	++	–	–	–	–	Mg, Q, Fs	Hryniv <i>et al.</i> (1993)	
3	++	++	–	–	–	–	Mg	Yaremchuk (2010)			
Halite	Badenian, Tyras	6	+	+	(+)	–	++	+	Do, (Q)	Iaremchuk and Hryniv (2008)	
		17	+	(+)	+	++	++	+	Do, Q, (Fs), Ca	Iaremchuk and Galamay (2009)	
	Vorotyshcha suite, Eger–Eggenburgian		10	++	++	–	–	–	+	Q, Fs, (Do)	Iaremchuk and Hryniv (2008)
	Badenian, Tereblya	Mukacheve Depression	10	++	+	–	+	++	–	Do, Ca, Q	Gabinet and Slyvko (1984)
			4	++	–	–	+	++	–	Do, Ca	Kityk <i>et al.</i> (1983)
		Solotvyna Depression	2; 2	++	++	–	–	–	–	Do, Ca	Bilonizhka (1979); Kityk <i>et al.</i> (1983)
			5	++	–	–	–	–	–	Mg, (Do)	Yarzhemskaya (1954)
	2	++	+	–	–	(+)	–	Q, Fs, (Do)	Yaremchuk (2010)		
Gypsum	Badenian, Tyras	12	++	+	+	–	(+)	(+)	Ca, Q	Bobrovnik and Karpenchuk (1969)	
		–	(+)	(+)	++			(+)		Bilonizhka (1990)	
		11	+	(+)	++	–	+	+	Ca, Do, Q, (Fs)	Iaremchuk and Poberezhskyy (2009)	

Clay minerals: It – illite; Ch – chlorite, Sm – smectite, mixed-layer clay minerals: Co* – chlorite-smectite of close-to-perfect order (corrensite), Ch-Sm – chlorite-smectite; It-Sm – illite-smectite; non-clay minerals: Q – quartz, Fs – feldspar, Do – dolomite, Ca – calcite, Mg – magnesite. The amount of mineral: ++ considerable; + minor; (+) admixture; – mineral not revealed.

Slyvko, 1984) in the Transcarpathian basin. Gypsum facies is characterized by smectite, illite, chlorite and mixed-layer minerals of chlorite-smectite and illite-smectite composition (Bobrovnik, Karpenchuk, 1969; Bilonizhka, 1990; Iaremchuk, Poberezhsky, 2009).

In this study, we analyze the literature data on clay minerals of evaporites of the Carpathian region of Ukraine in order to obtain a clear pattern of different-aged clay mineral assemblages, their formation and alteration in different facies of evaporite rocks.

GEOLOGICAL SETTING

Miocene evaporite deposits of the Carpathian region of Ukraine are located in the Carpathian Foredeep and Transcarpathian Trough (Fig. 1).

The Carpathian Foredeep in Ukraine is situated between the Folded Carpathians and East European Platform and ex-

tends from NW to SE as a 25–60-km wide and about 300-km long belt. It is subdivided into the Boryslav–Pokuttya, Sambir and Bilche–Volytsia zones (Vul *et al.*, 1998). The Boryslav–Pokuttya and Sambir zones have been thrust to the NE with amplitudes of 25 km and 8–12 km, accordingly. In the outer part of the Bilche–Volytsia Zone, Miocene deposits occur at the depth of 10–200 m. Towards the Folded Carpathians, they are gradually subsided under the overthrust of the Sambir Zone down to the depths of 1200–2200 m (Korenevskiy, Donchenko, 1963).

The Transcarpathian Trough is a sag structure formed at the boundary of the Folded Carpathians and the Pannonian Median Massif and is separated from them by deep faults. The second-order Khust fault divides the trough into the Solotvyna and Mukacheve depressions (Kityk *et al.*, 1983). In the central part of the Solotvyna depression, salt domes occur.

In the Carpathian Foredeep, Miocene evaporites occur in the Boryslav–Pokuttya (Vorotyshcha suite, Egerian–Eggenburgian), Sambir (Tyras suite, Badenian) and Bilche–Volytsia (Tyras suite, Badenian) zones (Hryniv *et al.*, 2007). In the Boryslav–Pokuttya and Sambir zones, evaporites are composed of saline clays and rock salt. In some areas they are represented by salt-bearing breccia with potash salts. The stratigraphic age of potash salts of the Kalush–Holyn' deposit is a topic for discussion (e.g. Wójtowicz *et al.*, 2003; Peryt, Hryniv, 2011); after Dzhinoridze *et al.* (1980) we consider it as Badenian. In the Bilche–Volytsia Zone, evaporites change their composition from gypsum and anhydrite (with clay, sandstone, limestone and marl seams) in the outer (NE) part to rock salt in the SW part. Studies of calcareous nanoplankton indicated that the evaporites belong to the NN6 Zone (Peryt, Peryt, 1994; Peryt, 1999; Andreyeva-Grigorovich *et al.*, 2003). In the Transcarpathian Trough, evaporites are located in both the Solotvyna and Mukacheve depressions (Tereblyia suite, Badenian) and are represented by rock salt with an admixture of clay, anhydrite and rare tuffs.

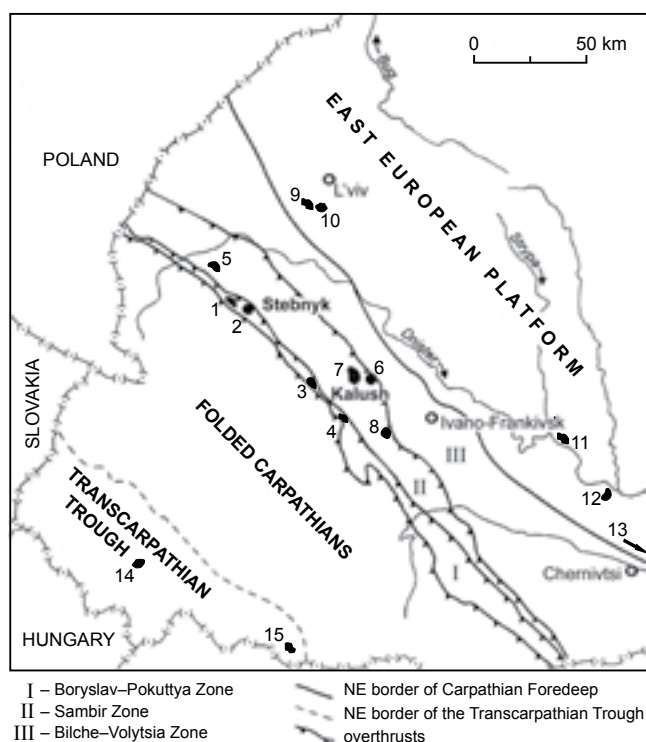


Fig. 1. Location of sampled sites, tectonic zonation of the Carpathian Foredeep after Vul *et al.* (1998)

Carpathian Foredeep: Boryslav–Pokuttya Zone: 1 – Boryslav, 2 – Stebnyk, 3 – Dolyna, 4 – Verkhniy Strutyn; Sambir Zone: 5 – Silets’–Stupnytsya, 6 – Kalush, 7 – Holyn’, 8 – Hrynivka; Bilche–Volytsia Zone and adjacent part of the East European Platform: 9 – Shchyrets’, 10 – Piski, 11 – Nagiryany, 12 – Verenchanka, 13 – Kryva; Transcarpathian Trough: 14 – Mukacheve, 15 – Solotvyna

MATERIAL AND METHODS

In the present study, we analyze and generalize XRD data on pelitic fraction mineralogy of water-insoluble residue from Miocene gypsum, rock salt and potash-bearing salts of the Ukrainian Carpathians region. The studied evaporites of the Carpathian Foredeep are of Badenian (Tyras suite) and Egerian–Eggenburgian (Vorotyshcha suite) age; Badenian samples come from the Bilche–Volytsia Zone and the ad-

acent part of the East European platform (gypsum) and the Sambir Zone (gypsum, rock salt and potash salts). Egerian–Eggenburgian samples are from the Boryslav–Pokuttya Zone (rock salt and potash salts). In the Transcarpathian Trough, clay minerals of rock salt from the Tereblyia suite (Badenian) were studied in both the Solotvyna and Mukacheve depressions (Fig. 1, Tab. 1).

The evaporites of the Carpathian Foredeep are of Badenian (Tyras suite) and Egerian–Eggenburgian (Vorotyshcha suite) ages. Badenian samples come from the Bilche–Volytsia Zone and the adjacent part of the East European platform (gypsum) and the Sambir Zone (gypsum, rock salt and potash salts). Egerian–Eggenburgian samples come from the Boryslav–Pokuttya Zone (rock salt and potash salts). In the

Transcarpathian Trough, clay minerals from rock salt of the Tereblyia suite (Badenian) were studied in both the Solotvyna and Mukacheve depressions (Fig. 1, Tab. 1).

In most of studies, the clay fraction of water-insoluble residue from evaporites was investigated by means of X-ray powder diffraction and, sometimes, thermal analysis.

CLAY MINERAL ASSEMBLAGES

In Neogene evaporites of the Carpathian region, the pelitic fraction from rocks of gypsum facies is represented by smectite, illite, chlorite and mixed-layer chlorite-smectite and illite-smectite (Fig. 2, Tab. 1) (Iaremchuk, Poberezhsky, 2009). Smectite is represented by two varieties – dioctahedral Al-Fe and trioctahedral Mg. Chlorite is of Mg-Fe composition. In gypsum facies, clay minerals are mostly allogenic (dioctahedral smectite, illite, chlorite), whilst authigenic clay minerals (trioctahedral smectite and illite) are present in insignificant amount.

The clay mineral association of halite facies of Egerian–Eggenburgian and Badenian rock salt of the Vorotyshcha suite differs by the number of clay minerals from the Tyras (Forecarpathian region) and Tereblyia (Transcarpathian region) suites (Fig. 3, Table 1). Illite and chlorite are present in all samples; most of samples from the Forecarpathian region also contain small amount of mixed-layer illite-smectite.

In the rock salt of the Vorotyshcha suite, illite and chlorite are present in considerable amounts. The small number of mixed-layer illite-smectite is present in all but two samples (in these two samples magnesite was also found). Admixture of mixed-layer chlorite-smectite was noted only twice (Iaremchuk, Hryniv, 2008).

In the rock salt of the Tyras suite, the illite and chlorite content is smaller than in that of the Vorotyshcha suite. In most of samples, mixed-layer chlorite-smectite with the admixture of illite-smectite was determined. In rock salt of the Silets’–Stupnytsya area, mixed-layer chlorite-smectite is present in considerable amount in all samples, smectite is in modest amount in most of samples, and corrensite was determined only once (Iaremchuk, Hryniv, 2008). In samples from the Hrynivka area (Iaremchuk, Galamay, 2009), swelling minerals (corrensite, smectite and mixed-layer chlorite-smectite) are usually found in considerable amount.

In rock salt of the Tereblyia suite (Mukacheve depression, Transcarpathian Trough), clay minerals are represented by illite and mixed-layer chlorite-smectite. The amount of latter is equal to those of illite or exceeds it; the amount of chlorite is insignificant, and smectite was absent (Kityk *et*

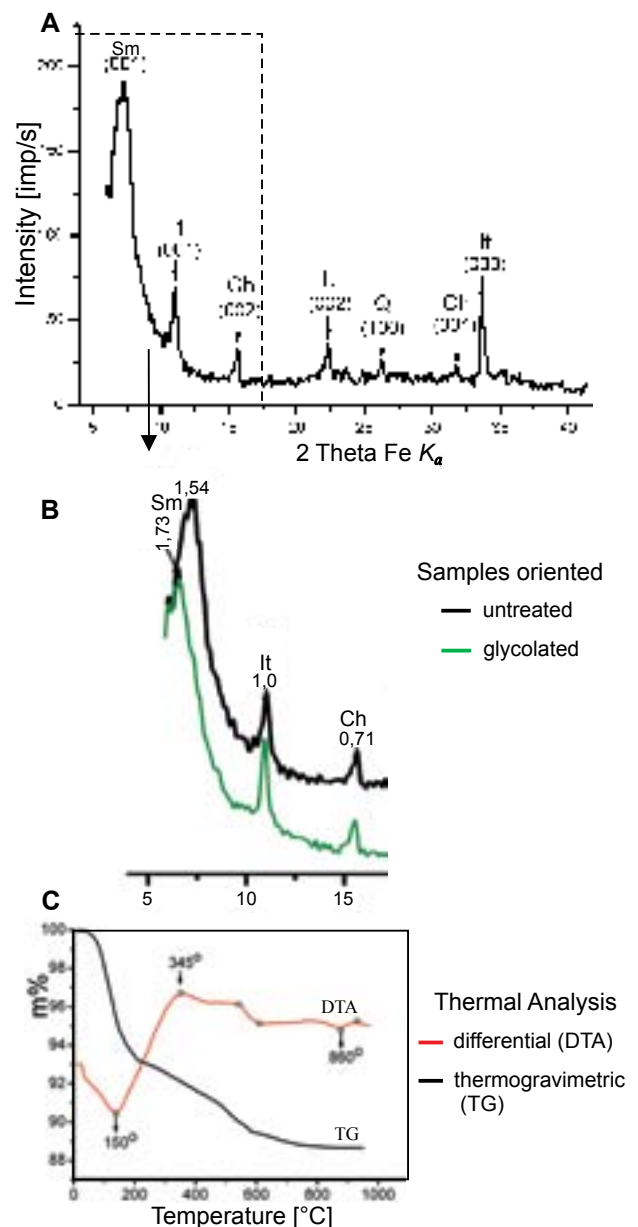


Fig. 2. XRD (A, B) and DTA-TG (C) data for pelitic fraction of water-insoluble residue from gypsums of outer part of the East European Platform

A – minerals: smectite (Sm), illite (It), chlorite (Ch) and quartz (Q); B – smectite reflection (001) 1.54 nm moved to 1.73 nm on ethylene glycol solvated preparations; C – endothermic peak of smectite dehydration (DTA pattern), with corresponding loss of water – about 6% (TG pattern)

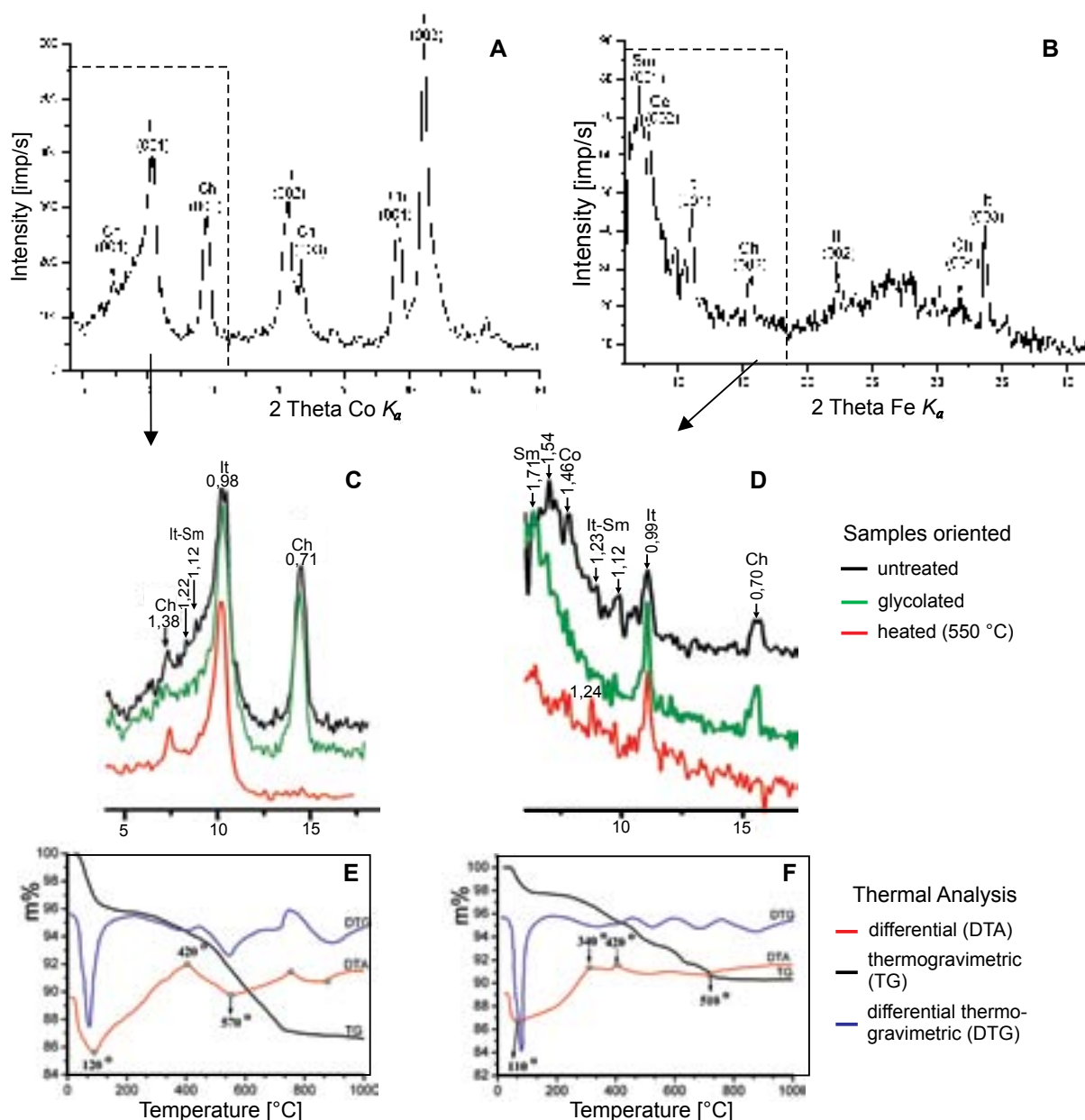


Fig. 3. XRD (A–D) and DTA-TG (E, F) for pelitic fraction of water insoluble residue of rock salt of the Boryslav–Pokuttya (A, C, E) and Sambir (B, D, F) zones of the Carpathian Foredeep

A – minerals: illite (It) and chlorite (Ch); C – on the X-ray diagrams, the (001) peak of illite is asymmetric, widening to small angles side, what could be caused by weak crystal structure (with interstratified water and/or swelling packets). This reflection has degraded form and series of low-intensity peaks, which evidence the presence of smectite packet in illite structure; E – endothermic peak of illite dehydration (DTA pattern), with corresponding loss of water – about 2% (TG pattern); B – minerals: smectite (Sm), corrensite (Co), illite (It) and chlorite (Ch); D – the mixed-layer illite-smectite is determined by small peaks 1.12–1.23 nm, which moved to 1.46 nm after ethylene glycol solvation. Smectite is determined by (001) reflection 1.54 nm, which moved to 1.71 nm on ethylene glycol solvated preparation and to 0.99 nm on ethylene treated preparation. The reflections of corrensite (well-ordered mixed-layer chlorite- smectite) on XRD pattern of oriented untreated preparation are at 1.46 nm, on ethylene glycol solvated preparation it moved to 1.60 nm, and on thermally treated preparation, the peak is close to 1.24 nm; F – endothermic peak of dehydration (DTA pattern), with corresponding loss of water – about 3% (TG pattern); insignificant loss of interlayer water is due to corrensite occurrence

al., 1983; Gabinet, Slyvko, 1984). In some cases, the mixed-layer chlorite-smectite structure is well-ordered (1:1), close to corrensite (Kityk *et al.*, 1983; Gabinet, Slyvko, 1984). In the Solotvyna depression (Transcarpathian Trough), rock salt of the Tereblyya suite contains illite and chlorite. The mixed-layer illite-smectite and chlorite-smectite are absent (Biloni-

zhka, 1979), or very insignificant admixture of mixed-layer illite-smectite is present (Yaremchuk, 2010), which is the typical feature of this suite.

Clay minerals of potash facie evaporites are represented only by illite and chlorite (Yarzhemskaya, 1954; Bilonizhka *et al.*, 1966; Bilonizhka, 1992a; Hryniv *et al.*, 1993; Oli-

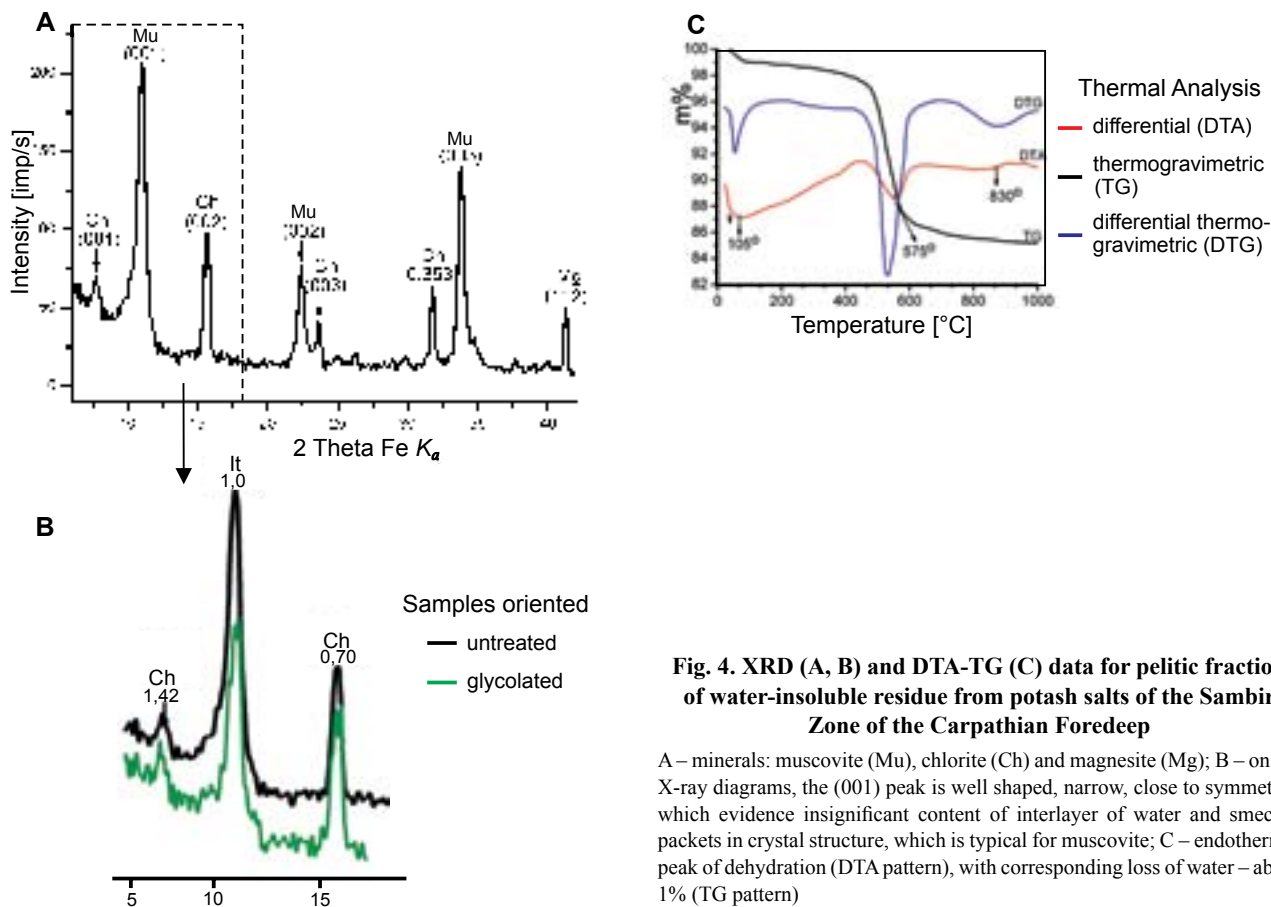


Fig. 4. XRD (A, B) and DTA-TG (C) data for pelitic fraction of water-insoluble residue from potash salts of the Sambir Zone of the Carpathian Foredeep

A – minerals: muscovite (Mu), chlorite (Ch) and magnesite (Mg); B – on the X-ray diagrams, the (001) peak is well shaped, narrow, close to symmetric, which evidence insignificant content of interlayer of water and smectite packets in crystal structure, which is typical for muscovite; C – endothermic peak of dehydration (DTA pattern), with corresponding loss of water – about 1% (TG pattern)

ovych *et al.*, 2004). Illite is characterized by good crystallization and absence of swelling layers – the (001) illite peak is narrow and symmetrical. XRD data are confirmed by complex thermal analyses (DTA-TG) (Fig. 4) – low-temperature endothermic peak, which reflects the dehydration of illite, is accompanied by insignificant loss of weight (1%), and the dehydroxylation is reflected by an endothermic peak maximum at 830°C. The shift of this endothermic peak to high

temperature (compared to those of illite) and low content of interlayer water allow determination of muscovite (Yaremchuk, 2010). Thus, the clay mineral assemblage of potash facies of the Forecarpathian evaporites consists of well-crystallized illite (sometimes authigenic muscovite) and chlorite.

In the clay fraction of all facies, there are traces of non-clay minerals – quartz, in some samples feldspar or dolomite, very seldom – calcite or magnesite.

TRANSFORMATION OF CLAY MINERALS IN MARINE HYPERSALINE SETTINGS

In marine evaporites, most of clay minerals are authigenic (Pastukhova, 1965). It is suggested that the hypersaline marine depositional environment played a major role in the genesis of the clay mineral assemblages (Bodine, 1983). Clay minerals in a hypersaline environment undergo transformations under the action of different factors. In continental saline lakes, transformation of clay minerals depends upon temperature and can be used as a paleoclimatic indicator (Calvo *et al.*, 1999). Lateral increase of salinity and alkalinity was the principal factor controlling the smectite to illite proportion in the Jurassic Lake T'oo'dichi', Morrison Formation (Turner, Fishman, 1991). Due to solution, chemistry changes within a concomitant lateral zonation of mixed-layer illite-smectite de-

veloped, from highly smectitic in the outermost zones to highly illitic in the central zone (Turner, Fishman, 1991). The impact of salinity on the degree of smectite to illite transformation in salt-bearing bentonites of the East Slovak basin did not reveal itself during sedimentation; but salinity may enhance it when combined with a higher burial temperature (Uhlik *et al.*, 2002; Honty *et al.*, 2004). Experimental study of K-saturated bentonites subjected to multiple wetting and drying cycles (Honty *et al.*, 2003) showed that NaCl concentration in solutions does not have straightforward effect of K fixation by smectites. It seems that in saline depositional settings the solution chemistry is a principal factor controlling the smectite to illite proportion (Warren, 2006).

Experimental study of conditions of clay minerals transformation (Frank-Kamenetskiy *et al.*, 1983) showed that the main factors are pressure, temperature, porosity and the contents of K, Na, Ca and Mg chlorides in pore solutions. Some clay minerals (smectite, kaolinite and mixed-layer ones) are unstable in hypersaline conditions and they undergo transformations under the impact of evaporite basin brines (Frank-Kamenetskiy *et al.*, 1983; Drits, Kossovskaya, 1990). Allogenic dioctahedral smectite, brought to the evaporite basin by runoff waters, was then transformed into di- and trioctahedral smectites, which transform through the mixed-layer illite-smectite into dioctahedral illite or through chlorite-smectite into trioctahedral chlorite. This transformation takes place due to K and/or Mg cations fixation by inter-layer intervals of smectite due to clay mineral structure ordering. Kaolinite transforms into dioctahedral illite through dioctahedral Al-smectite, and then through mixed-layer illite-smectite (Frank-Kamenetskiy *et al.*, 1983). Volcanic glass of pyroclastic material is also unstable under hypersaline conditions and transforms into trioctahedral smectite, which, in turn, transforms to chlorite through corrensite and mixed-layer chlorite-smectite (Drits, Kossovskaya, 1990).

The high content of clays is a typical feature of the Forecarpathian evaporites so a considerable amount of terrigenous clays were carried to the studied Miocene basins by runoff. Clay mineral composition of the underlying deposits differs from that of evaporites by the presence of kaolinite and smectite (Bilonizhka, 1979; Hryniv *et al.*, 1993). Evidently, those minerals were also carried into the evaporite basin, but did not persist in a saline environment and through the several intermediate phases have been transformed into illite and chlorite (Frank-Kamenetskiy *et al.*, 1983; Bilonizhka, 1992b). The Transcarpathian volcanic activity of Badenian age supplied pyroclastic material to the evaporite basins. This is proved by thin layers of volcanic tuff and tuffite in Badenian evaporites of Ukraine (Korenevskiy, 1954; Dzhi-noridze *et al.*, 1974) and Poland (Bukowski, 1999; Dudek *et al.*, 2004) and is recorded in a specific clay mineral composition of rock salt of the Tyras and Tereblya suites. The additional evidence in favour of volcanic material supply to the Badenian Forecarpathian evaporite basin is the presence of analcime (Iaremchuk, Galamay, 2009) in the silty-pelitic fraction of water-insoluble residue of Hrynivka, since analcime is believed to be the product of volcanic glass alteration (Deer *et al.*, 1966).

The analysis of published data shows that intensity of clay minerals transformation in evaporites of the Carpathian region depends on basin brine concentration. In gypsum facies, the transformation processes are weak and clay minerals are mostly allogenic. In halite facies, these processes are clear and intermediate minerals such as smectite and mixed-layer phases are present. In potash salt facies, stable minerals (illite and chlorite) are only found.

The **gypsum facies** deposits (Badenian gypsum) of the Carpathian region were deposited in shallow-water conditions from concentrated seawater, which was partly diluted by continental runoff (Peryt, 1996; Peryt *et al.*, 1997, 2010).

Low K and Mg concentrations in brines conditioned slow transformation of unstable clay minerals. This is why the pelitic fraction of water-insoluble residue consists mainly of allogenic minerals – dioctahedral smectite, illite and chlorite.

In **halite facies** deposits, clay mineral assemblages of rock salt contain mixed-layer minerals, illite and chlorite. Mixed-layer minerals are the transition phases of smectite and kaolinite transformation, while illite and chlorite are represented by both allogenic and authigenic components. These mineral transformation processes have not been completed due to lower brine concentration. This causes the presence of intermediate mixed-layer phases revealed in both Egerian–Eggenburgian and Badenian rock salt. Different assemblages of swelling Mg-minerals (mixed-layer chlorite-smectite, corrensite and smectite) are present in all studied Badenian rock salt. These minerals are the products of pyroclastic material alteration.

According to Kossovskaya *et al.* (1975) and Sokolova (1982), smectite, corrensite and mixed-layer chlorite-smectite are characteristic for gypsum facies. Significant amount of these minerals in rock salt of the Tyras and Tereblya suites is caused not only by Badenian volcanic activity and by basin brine concentration which was quite low (beginning of the halite stage) (Iaremchuk, Galamay, 2009).

When brine concentration increases even up to the end part of the halite stage, mixed-layer minerals do not occur. In two samples of rock salt from the Vorotyshcha suite (top part of borehole 17Dr, Boryslav area), mixed-layer illite-smectite is lacking (Iaremchuk, Hryniv, 2008). It is caused by a higher brine concentration, which is confirmed by the presence of magnesite in the same samples (according to Bilonizhka, 1985, magnesite proves the higher stage of evaporation) and by the occurrence of potash salts in the Boryslav area.

The difference between the clay mineral assemblages of Badenian rock salt from Hrynivka and Silets'–Stupnytsya is also caused by variations in brine concentration in these areas. In the Hrynivka area (Iaremchuk, Galamay 2009), the lower brine concentration (beginning of the halite stage) favoured preservation of smectite, corrensite and mixed-layered chlorite-smectite. Rock salt from the Silets'–Stupnytsya area is composed of halite that precipitated mostly from low-concentration brines, and only sometimes the basin brines reached the end of halite stage of evaporation (Iaremchuk, Hryniv, 2008). Occasional high concentration is also evidenced by 25–30 cm polyhalite layer in borehole 348 (Petrichenko *et al.*, 1974). As a result of increased brine concentration in rock salt of this area, corrensite is lacking and smectite is present in minor amount.

The clay mineral assemblage in rock salt of the Soltovyna depression is different from the rest of the Badenian deposits, because here the rock salt contains mainly illite and chlorite. This is strange taking into account that Badenian volcanoes, which supplied pyroclastic material to evaporite basins of Transcarpathia and Forecarpathia, were located not far from the Soltovyna depression (Korenevskyy, 1954).

Rock salt of the Soltovyna depression precipitated from brines of quite high concentration – the end of halite stage. However, mixed-layer minerals are present in some samples of rock salt from Silets’–Stupnytsya in spite of similar concentration. The temperature in the Soltovyna depression did not exceed 40°C (Kityk *et al.*, 1983), so it did not affect the processes of mineral transformation. The possible explanation is insignificant input of pyroclastic material to this part of the Badenian evaporite basin due to specific wind direction.

Similar composition of clay minerals from rock salt facies is observed in Badenian evaporites of the Carpathian region outside Ukraine. Smectite and mixed-layer illite-smectite with illite, chlorite and kaolinite occur also in Badenian rock salt deposits of Wieliczka, Poland (Langer-Kuźniarowa *et al.*, 2002) and in the Transylvanian basin, Romania, where they are accompanied by minor amounts of other clay minerals (Bican-Brisan, Hosu, 2006).

At a high degree of evaporation – in potash salt facies, the unstable clay minerals fully transform and only illite and chlorite occur in potash salts of the Vorotyshcha and Tyras suites (Bilonizhka, 1992a).

The effect of temperature on clay minerals transformation in hypersaline settings reveals itself during both sedi-

mentation (Calvo *et al.*, 1999) and burial at a higher temperature (Uhlik *et al.*, 2002; Honty *et al.*, 2004). Under progressive salinization in a marine evaporite basin, not only concentration of brines, but also the temperature increase. Thus, according to fluid inclusion studies, brine temperature in Miocene evaporite basins of the Carpathian region did not exceed 40°C for halite facies, and it reached 60°C for potash salt facies (Petrichenko, 1988). Burial temperatures probably were not higher; otherwise, they would be recorded by halite-hosted fluid inclusions due to halite ability to easily recrystallize. In the Mukacheve depression, the burial temperature reached 75–83°C (Petrichenko, 1989) and fluid inclusions in halite have gas bubbles in contrast to the Soltovyna depression where the burial temperatures were not so high. However, the clay mineral assemblage from the Mukacheve depression contains mixed-layer minerals not observed in the Soltovyna depression (although this is the Soltovyna depression where the occurrence of mixed-layer clay minerals is expected). To our opinion, all this evidences that it was brine concentration that formed clay mineral composition, while the temperature (either basin brine or burial) was too low to affect the clay mineral assemblages of the Carpathian region.

CONCLUSIONS

All data on clay minerals of Miocene evaporites from the Carpathian region show decrease in the amount of swelling minerals and the better ordering of the clay mineral structure with the increase of basin brines concentration. Gypsum deposits contain mainly allogenic clay minerals: dioctahedral smectite, illite and chlorite, characteristic for relatively low brine concentration, and minor amount of authigenic minerals – trioctahedral smectite and illite – evidence of the onset of mineral transformation under brine influence. In halite deposits, illite, chlorite and mixed-layer illite-smectite are present. Rock salt of the Tyras and Tereblyia suites contains also smectite, corrensite and mixed-layer chlorite-smectite. Such a mineral assemblage is caused by Badenian volcanic activity – pyroclastic material supply to the evaporite basin and its transformation in

a saline environment. The chlorite and illite association in pelitic fraction of evaporites of potash salt facies evidence the termination of unstable clay minerals, and the ordering of the illite structure sometimes even resulted in the occurrence of authigenic muscovite.

Changes in clay mineral assemblages (vanishing of swelling minerals and structure ordering) in evaporites of the Carpathian region were caused by an increase of concentration of basin brines which is in accordance with the conclusions about transformations of clay minerals in evaporite basins (Frank-Kamenetskiy *et al.*, 1983; Bilonizhka, 1992b). Volcanic activity had also strong impact on clay minerals composition – pyroclastic material alteration results in the occurrence of smectite, corrensite and mixed-layer chlorite-smectite.

REFERENCES

- ANDREYEVA-GRIGOROVICH A.S., OSZCZYPKON., SAVITSKAYA N.A., ŚLĄCZKA A., TROFIMOVICH N.A., 2003 — Correlation of Late Badenian salts of the Wieliczka, Bochnia and Kalush areas (Polish and Ukrainian Carpathian Foredeep). *Ann. Soc. Geol. Pol.*, **73**: 67–89.
- BICAN-BRISAN N., HOSU A., 2006 — Clay mineral association in the salt formation of the Transylvanian basin and its palaeo-environmental significance. *Studia UBB, Geologia*, **51**, 1–2: 35–41.
- BILONIZHKA P.M., 1979 — O mineralnom sostave karbonatov i glin Soltovinskogo mestorozhdeniya kamennoy soli (Zakarpattia). *In: Voprosy geologii i geokhimii solenosnykh otlozheniy* (ed. V.I. Kityk): 53–61. Naukova Dumka, Kiev [in Russian].
- BILONIZHKA P.M., 1985 — Magnezit galogennykh otlozheniy Predkarpatya, ego geneticheskoye i poiskovoye znachenie. *In: Evapority Ukrainy* (ed. V.I. Kityk): 67–73. Naukova dumka, Kiev [in Russian].
- BILONIZHKA P.M., 1990 — Glinistyie mineraly tortonskikh i nizhnesarmatskikh otlozheniy Predkarpatya. *Mineralogicheskii sbornik*, **44**, 2: 99–104 [in Russian].
- BILONIZHKA P.M., 1992a — The clay minerals as indicators of salt deposition conditions in Precarpathian Foredeep. *Geologi-*

- ya i geokhimiya horiuchykh kopalyn, **78**, 1: 95–102 [in Ukrainian, English abstract].
- BILONIZHKA P.M., 1992b — The transformation of terrigenous clay minerals in the saliferous process. *Mineralogichnyy zbirnyk*, **45**, 2: 51–56 [in Ukrainian, English abstract].
- BILONIZHKA P.M., VYNAR O.N., MELNIKOV V.S., 1966 — O mineralnom sostave glin solianykh porod kaliynykh miestorozhdeniy Prikarpatya. *Voprosy mineralogii osadochnykh obrazovaniy*, **7**: 147–158 [in Russian].
- BOBROVNIK D.P., KARPENCHUK U.R., 1969 — Lithology and mineralogy of the Upper Tortonian deposits of the Tiras Suite of the Inner Zone of the Precarpathian Depression. *In: Voprosy litologii i petrografii*. **1**: 46–56. Izdatelstvo Lvovskogo universiteta, Lvov [in Russian, English abstract].
- BODINE M.W.JR., 1983 — Trioctahedral clay mineral assemblages in Paleozoic marine evaporite rocks. Sixth Intern. Symp. on Salt. **1**: 267–284.
- BUKOWSKI K., 1999 — Porównanie badeńskiej serii solonośnej z Wieliczki i Bochni w świetle nowych danych. *Pr. Państw. Inst. Geol.*, **58**: 43–56.
- CALVO, J.P., BLANC-VALLERON M.M., RODRIGUEZ ARANDIA J.P., ROUCHY J.M., SANZ M.E., 1999 — Authigenic clay minerals in continental evaporitic environments: *Intern. Assoc. Sediment. Spec. Publ.*, **27**: 129–151.
- DEER W.A., HOWIE R.A., ZUSSMAN J., 1966 — Rock-forming minerals. Vol. 3, Sheet Silicates. Longmans, London.
- DRITS V.A., KOSOVSKAYA A.G., 1990 — Glinistyne mineraly: smektity, smeshanosloynnye obrazovaniya. Nauka, Moskva [in Russian].
- DUDEK K., BUKOWSKI K., WIEWIÓRKA J., 2004 — Datowanie radiometryczne badeńskich osadów piroklastycznych z okolic Wieliczki i Bochni. *Materiały VIII Ogólnopolskiej Sesji Naukowej „Datowanie minerałów i skał”*: 18–19.
- DZHINORIDZE N.M., GEMP S.D., GORBOV A.F., RAYEVSKIY V.I., 1980 — Zakonomernosti razmeshcheniya i kriterii poiskov kaliynykh soley SSSR. Metsniereba, Tbilisi [in Russian].
- DZHINORIDZE N.M., ROGOVA M.S., TELEGIN V.P., 1974 — Vulkanogennnye porodny Kalush-Golynskogo mestorozhdeniya kaliynykh soley. *Trudy Vsesoyuznogo instituta galurgii*, **71**: 36–56 [in Russian].
- FRANK-KAMENETSKIY V.A., KOTOV N.V., GOYLO T.L., 1983 — Transformatsionnye preobrazovaniya sloistykh silikatov. Nedra, Leningrad [in Russian].
- GABINET M.P., SLYVKO E.P., 1984 — Clay minerals from rock salt of the Svalyava region in Transcarpathia. *Mineralogicheskyy sbornik*, **38**, 1: 56–62 [in Russian, English abstract].
- HONTY M., ŠUCHA V., PUŠKELOVA L., 2003 — Potassium fixation in smectites by wetting and drying in NaCl solution. *Geol. Carpath.*, **54**, 4: 261–264.
- HONTY M., UHLÍK P., ŠUCHA V., ČAPLOVIČOVA M., FRANČU J., CLAUER N., BIRŇ A., 2004 — Smectite-to-illite alteration in salt-bearing bentonites (East Slovak Basin). *Clay and Clay Minerals*, **52**: 533–551.
- HRYNIV S.P., DOLISHNIY B.V., KHMELEVSKA O.V., POBEREZHSKY A.V., VOVNYUK S. V., 2007 — Evaporites of Ukraine: A review. *Geol. Soc. London, Spec. Publ.*, **285**: 309–334.
- HRYNIV S.P., KORIN' S.S., BILONIZHKA P.M., 1993 — The use of clay minerals and carbonates for clarification of geological structure peculiarities of Stebnyk potash salt deposit. *Geologiya i geokhimiya horiuchykh kopalyn*, **82**, 1: 47–82 [in Ukrainian, English abstract].
- IAREMCHUK IA.V., GALAMAY A.R., 2009 — Mineral composition of the water insoluble residue from rock salt Hrynivka area of the Carpathian Foredeep. *Geologiya i geokhimiya horiuchykh kopalyn*, **1**, **146**: 79–90 [in Ukrainian, English abstract].
- IAREMCHUK IA.V., HRYNIV S.P., 2008 — Clay minerals in the rock salt of Miocene evaporites of the Carpathian region, Ukraine. Recent problems of lithology and mineralogenesis of sedimentary basins of Ukraine and adjacent territories (eds. P.F. Hozhyk et al.): 209–215. LOGOS, Kyiv [in Ukrainian, English abstract].
- IAREMCHUK IA.V., POBEREZHSKY A.V., 2009 — Clay mineral composition of Badenian gypsum of the Dnister river region. *Mineralogichnyy zbirnyk*, **59**, 1: 116–127 [in Ukrainian, English abstract].
- IVANOV A.G., APOLLONOV V.N., BORISENKOV V.I., 1980 — Mineralnye paragenezы galopelitov v otlozheniyakh kaliynykh soley. *Doklady AN SSSR*, **253**, 2: 469–472 [in Russian].
- KITYK V.I., BOKUN A.N., PANOV G.M., SLIVKO E.P., SHAID-ETSKAYA V.S., 1983 — Galogennnye formatsii Ukrainy: Zakarpatskiy progib. Naukova Dumka, Kiev [in Russian].
- KORENEVSKIY S.M., 1954 — Miotsenovyye vulkanicheskie tuffy Predkarpatia. *Trudy Vsesoyuznogo instituta galurgii*, **29**: 176–196 [in Russian].
- KORENEVSKIY S.M., DONCHENKO K.B., 1963 — Geologiya i usloviya formirovaniya kaliynykh otlozheniy Sovetskogo Predkarpatia. *Trudy Vsesoyuznogo geologicheskogo instituta N.S.*, **99**: 3–153 [in Russian].
- KOSOVSKAYA A.G., SOKOLOVA T.N., DRITS V.A., SAKHAROV B.A., 1975 — Paragenezы i istoriya formirovaniyaglinistykh mineralov v basseynakh nachalnoy stadii evaporitovoy sedimentatsii. *In: Problems of litology and geochemistry of sedimentary rocks and ores* (eds. A.V. Peive et al.): 278–296. Nauka, Moskva [in Russian].
- LANGIER-KUŹNIAROWA A., CEBULAK S., STARNAWSKA E., CZAPOWSKI G., 2002 — Mineral composition of mixed clay-salt deposits (zuber) from the Neogene (Upper Badenian) succession of the Polish Carpathian Foredeep. *Mineralogichnyy zbirnyk*, **52**, 2: 101–105 [in English].
- OLIYOVYCH O., YAREMCHUK YA., HRYNIV S., 2004 — Clays of saliferous deposits and weathering zone of Kalush-Holyn' potash salt deposit (Miocene, Forecarpathia). *Mineralogichnyy zbirnyk*, **54**, 2: 214–223 [in Ukrainian, English abstract].
- PASTUKHOVA M.V., 1965 — K poznaniyu autigennykh silikatnykh i aliumosilikatnykh mineralov v solenosnykh porodakh. *Litologiya i poleznye iskopaemye*, **3**: 78–90 [in Russian].
- PERYT D., 1999 — Calcareous nannoplankton assemblages of the Badenian evaporites in the Carpathian Foredeep. *Biul. Państw. Inst. Geol.*, **387**: 158–161.
- PERYT T.M., 1996 — Sedimentology of Badenian (Middle Miocene) gypsum in eastern Galicia, Podolia and Bukovina (West Ukraine). *Sedimentology*, **43**: 571–588.
- PERYT T.M., HRYNIV S., 2011 — On strontium isotope composition of Miocene potash evaporites in the Ukrainian Carpathian Foredeep. *Geologiya i geokhimiya horiuchykh kopalyn*, **156–157**, 3–4: 81–95 [in English].

- PERYT T.M., PERYT D., 1994 — Badenian (Middle Miocene) Rattyn Limestone in western Ukraine and northern Moldavia: microfacies, calcareous nannoplankton and isotope geochemistry. *Bull. Pol. Acad. Sc. Earth Sci.*, **42**: 127–136.
- PERYT T.M., HAŁAS S., KAROLI S., PERYT D., 1997 — Zapis izotopowy zmian środowiskowych podczas depozycji gipsów badenijskich w Koberżycach koło Opawy. *Prz. Geol.*, **45**, 8: 807–810.
- PERYT T.M., HRYNIV S.P., ANCKIEWICZ R., 2010 — Strontium isotope composition of Badenian (Middle Miocene) Calcium sulphate deposits in West Ukraine: a preliminary study. *Geol. Quart.*, **54**, 4: 465–476.
- PETRICHENKO O.I., 1988 — Fiziko-khimicheskie usloviya osadkoobrazovaniya v drevnikh solerodnykh basseynakh. Naukova Dumka, Kiev [in Russian].
- PETRICHENKO O.I., 1989 — Epigenez evaporitov. Naukova Dumka, Kiev [in Russian].
- PETRICHENKO O.I., KOVALEVICH V.M., TCHALYY V.N., 1974 — Geokhimicheskaya obstanovka soleobrazovaniya v tortonskom evaporitovom basseynie severo-zapadnogo Predkarpattya. *Geologiya i geokhimiya goriuchih iskopaemyh*, **41**: 74–80 [in Russian].
- SOKOLOVA T.N., 1982 — Autigennoye silikatnoye mineraloobrazovanie raznykh stadiy osolonieniya. Nauka, Moskva [in Russian].
- TURNER C.E., FISHMAN N.S., 1991 — Jurassic Lake T'oo'dichi: A large alkaline, saline lake, Morison Formation, eastern Colorado Plateau. *Geol. Soc. Amer. Bull.*, **103**, 4: 538–558.
- UHLÍK P., HONTY M., ŠUCHA V., FRANČŮ J., BIRŮŇ A., CLAUER N., HANZELYOVÁ Z., MAJZLAN J., 2002 — Influence of salt-bearing environment to illitization. In: Proceedings of the XVII Congress of CBGA Bratislava, *Geol. Carpath.*, **53**, CD-ROM.
- VUL M.Y., DENEGA B.I., KRUPSKYY Y.Z., NIMETS M.V., SVYRYDENKO V.G., FEDYSHYN V.O. (Eds.) 1998 — Western oil-and-gas-bearing regions. Vol. IV. In: Atlas of oil and gas fields of Ukraine, in six volumes. Vydavnytstvo Tsentru Europy, Lviv.
- WARREN J.K., 2006 — Evaporites: sediments, resources and hydrocarbons. Springer-Verlag, Berlin, Heidelberg.
- WÓJTOWICZ A., HRYNIV S.P., PERYT T.M., BUBNIK A., BUBNIAK I., BILONIZHKA P.M., 2003 — K-Ar dating of the Miocene potash salts of the Carpathian Foredeep (West Ukraine): application to dating of tectonic events. *Geol. Carpath.*, **54**, 4: 243–249.
- YAREMCHUK Ya.V., 2010 — Clay minerals of Phanerozoic evaporites as indicators of secular variation in seawater chemistry. Lviv [manuscript – in Ukrainian, English abstract].
- YARZHEMSKAYA E.A., 1954 — Veshchestvennyy sostav galopelitov. *Trudy Vsesoyuznogo instituta galurgii*, **29**: 260–314 [in Russian].