Carbonate and siliceous rock horizons at the boundary of Eocene and Oligocene deposits in the Ukrainian Carpathians as geotourism sites

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Abstract. The outcrops of carbonate and siliceous rock horizons at the boundary of Eocene and Oligocene deposits in the Ukrainian Carpathians represent potential sites for geotourism. They are located in the northern part of the Skyba zone, in settlements (Boryslav, Verkhne Synyovydne, Maydan, Skole) that can be reached by various vehicles. The sites are of interest not only due to the possibility to be shown for tourists in situ but also due to the possibility to tell them about sedimentological history of the Carpathians, the whole Tethys basin and the World Ocean being the reason for their formation. The article considers global and regional events at the Eocene-Oligocene boundary, exemplified by deposits of the Sheshory horizon and lower siliceous horizon of the Lower Menilite Sub-Formation as well as sedimentological and lithogenetic aspects of cherts origin. In sections of the Carpathian flysch the clay-calcareous and siliceous-clay rocks of the Sheshory (Eocene) and Rybnyk (Oligocene) horizons are overlaid by a pack of carbon-bearing cherts (mainly phthianites) of the Menilite Formation lower siliceous horizon. This was fixed as the «Eocene final event» (climatic cooling, mass extinction of some groups of marine organisms, including certain types of warm-water foraminifera), and had a global significance. At that time at the regional scale separation of the Paratethys Sea from the Tethys Ocean as well as sharp change in biogenic sedimentation (from carbonate to siliceous) in the Carpathian sedimentary basin occurred. At the Eocene and Oligocene boundary and then during the Oligocene the World Ocean demonstrated a series of events that ultimately led to the transformation of a global system of ocean waters circulation from the Cretaceous-Eocene, marked with uniformly warm climate throughout the planet, to contemporary with more contrast climate and distinct climatic zones. The change of warm-water plankton organisms for those who are accustomed to live in cold seas can be illustrated by the results of study of calcareous and siliceous rocks of the Eocene-Oligocene deposits in the Ukrainian Carpathians. The Sheshory horizon marls are composed of cryptocrystalline clay-carbonate matter with numerous remains of warm-water forms of planctonic foraminifera (Globigerinida) sized up to 0.1 mm. The number and size of these organisms significantly reduced in the rocks of Rybnyk horizon. No their traces are found in siliceous formations. Various researchers have justified biogenic, volcanogenic, or chemogenic origin of these cherts. Authors of the article believe that these rocks are the product of sedimentation of biogenic siliceous deposits and their post-sedimentary transformation.

Key words: Eocene, Oligocene, biotic crisis, cherts, Ukrainian Carpathians.

Horizonty karbonatnyh i kremeniystykh porid na kontakti eocenevych ta ologeoценowych vіdkladіv Ukrainsьких Карпат – об’єкти для геотуризму

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Анотація. Як потенційні об’єкти для геотуризму пропонуються відслонення порід карбонатних і кременистих горизонтів на контакті еоценових та олігоценових відкладів Українських Карпат. Вони знаходяться в північній частині Скібської зони, в населених пунктах, доступних для під’їзду різними видами автомобільного транспорту (м. Борислав, Верхнє Синьовиїдне, Майдан, Сколе). Ці об’єкти цікаві не тільки тим, що їх можна показати туристам на місцезнаходження, а й розказати про події в седиментологічній історії не тільки Карпатського, а й всього Тетису басейну і Світового океану, які були причиною їх формування. На прикладі відкладів шешорського горизонту і нижнього кременистого горизонту нижньокомілійської підсвіти розглянути глобальні та регіональні події на межі еоценового і олігоценового часу, а також седиментологічні і літогенетичні аспекти проблеми походження силіцитів. В розрізах карпатського флюїду, де глинисто-карбонатні і кременисто-глинисті породи шешорського (еоцен) і рибницького (олігоцен) горизонтів перекриваються кількометровою пачкою вуглецьвмісних

363
Introduction

The sequence of Cretaceous-Palaeogene flysch deposits of the Ukrainian Carpathians contains carbonate and siliceous rock horizons specific for their stratigraphically identifying significance. They record very interesting sedimentological events that occurred in the Carpathian basin as well as in the Tethys basin and the World Ocean. Primarily, these are the changes incontinents’ location and, accordingly, paleo-oceanographic situation. These changes entailed alteration of the system of ocean flows and change of climate, establishment of anoxic reducing environments (so-called «oceanic anoxic events») in sedimentary basins, biotic crises (extinction of certain marine organisms groups). The problem of siliceous rocks (cherts or silicites) genesis is controversial. Various researchers have justified biogenic, volcanogenic, or chemogenic origin of these rocks. Due to their strength, cherts outcrops are clearly expressed in the relief, forming cliffs on mountain slopes and also knickpoints and small waterfalls in the mountain rivers. They are of interest because not only tourists can see them in situ, but also a guide can tell them about events in the history of the Carpathians geological evolution, which were the cause of their formation.

Issues of the Carpathian geology have persistently been the subject of scientific discussions. In particular, the results of the sedimentological and litho-geochemical study of the Ukrainian Carpathians Eocene and Oligocene deposits are reflected in the works of the famous Carpathian geologists (Afanasieva, 1983, Gabinet, 1985, Koltun, 1989). Our articles (Popp, 1995, Popp, Senkovsky, 1996, 2003, Popp et al, 2004a, Senkovsky, Popp, 2010, Senkovsky et al, 2012, 2018) are dedicated to the study of siliceous rocks (cherts). The article (Popp et al, 2004b) is dedicated to the lithological, petrographic, and geochemical study of siliceous and carbonate rocks located in the stratigraphic boundary zone between the Upper Eocene deposits and black bituminous sequence of the Lower Menilite Sub-Formation.

The Sheshory horizon globigerina marls (Upper Eocene) and the siliceous rocks (cherts) of the Lower Menilite lower siliceous (lower «rohovyk» («hornfels»)) horizon is proposed as potential sites for geo-tourism. The study area is located in the central part of the Skyba zone of the Ukrainian Carpathians. We have studied them in the field within the central part of the Ukrainian Carpathians Skyba zone, in particular along the Tysmenytsia river in the vicinity of Boryslav (Beregova skyba), along the Opir river in the vicinity of Verkhnye Syniovydne (Oriv skyba), Skole (Skoleskyba) and the Rybnik river near the village Maydan (Parashka skyba) (Fig.1–3).

Fig. 1. Research area geographical location.

The specified Eocene and Oligocene rock outcrops are regularly shown during geological excursions organised for participants of scientific conferences and students of geological faculties. However, they are under-used as a geo-touristic object. Sedimentary deposits, studied by a geologist in order to reproduce the Carpathians, may be interesting for tourists as well. For instance, since siliceous rocks (cherts) are clearly visible in the relief and form waterfalls, they attract the attention of people who are not professional geologists. The most investigative one raises the following question: How could such rocks beformed during geological processes? Moreover, the above-mentioned changes in paleoenvironmental and paleoclimatological situations caused the global biotic crisis, the first one after the
extinction of dinosaurs and other giant reptiles at the end of the Mesozoic, which occurred at the Eocene and Oligocene boundary. To some extent, the above events have been reflected in the geological section of the Carpathians sedimentary complexes. It should be noted, that problem of geological disasters and mass extinction in the history of the Earth is particularly relevant in connection with the environmental problems that humanity faces with.

This article is focused on the horizons of the Upper Eocene carbonate rocks and the Lower Oligocene siliceous rocks both as potential sites for geological tourism and as evidences of certain paleoecological changes in the history of the Carpathian sedimentation basin. The reader’s attention is focused also on the origin of the cherts and on the events on a global and regional scale that took place at the Eocene-Oligocene boundary. General-audience presentation of the article allows to summarise briefly various views on the issue of silicates’ origination and information on global and regional events taken place at the Eocene and Oligocene boundary.

Results

Lithological characteristics of rocks in the zone of the Eocene and Oligocene deposits stratigraphic boundary and proposed sites for geological tourism. The Sheshory horizon of globigerina marls (from 10–20m to 40m) is preserved regionally in all structural-facial zones of the Carpathians at the top of Bystrytsya Formation and its facial analogs. It is represented by the alternated black and greenish-grey claystones, grey marls, and sandstones. In the Western Carpathians, the Sheshory horizon is known as the «globigerin marls». It is overlapped by siliceous-clayey rocks of the Rybnytsya (under-»rohovyk» («hornfels»)) horizon, developed at the base of the Lower Menilite sub-suite. There is a lower siliceous («lower «rohovyk» («hornfels»)) horizon of the Menilite deposits (up to 18–20 m) above, represented mainly with dark grey and black carbon-bearing quartz-chalcedony cherts (phthanites), and with calcareous cherts in its upper part. (Popp, Senkovsky, 2003, Popp et al, 2004b, Vialov et al, 1987, 1988) (Fig. 4).
There is a regular bus service from Boryslav to the regional center of Lviv and the resort city of Truskavets. Highways Skhidnytsia-Drohobych and Truskavets-Sambir pass through Boryslav. From Boryslav to Drohobych there is a railway laid, which presently operates mainly in a cargo-mode. The resort town of Skhidnytsia and the National Park «Skolivski Beskydy» are located to the south of Boryslav.

Boryslav sits at the foothills and on the northeastern slopes of the Ukrainian Carpathians (Eastern Beskydy) and in the intermontane basin on the Tismenytsia River. The border between the folded area of the Flysch Carpathians and the Carpathian Foredeep passes through Boryslav. The Boryslav oil field is located within the Skyba and Boryslav-Pokutian nappes thrust over the Carpathian Foredeep filled with molasses. The black bituminous shales sequence of the Menilite Formation («menilite shales») are the primary source of oil. The «Boryslav sandstone» is oil-bearing and forms a large lens in the Rybnytsya horizon rocks.

The complete section of Palaeogene flysch is observed in the vicinity of Boryslav, downstream of the river Tysmenytsia from the bridge on the road Boryslav-Skhidnytsia. Some time ago there was Mrazhnytsya village, which now has become the southwestern outskirts of the city. Houses, industrial premises and oil-production facilities are located on the left bank of the river (Fig. 5).

Boryslav Palaeogene section is a stratigraphic (geological) monument belonging to the national reserve fund sites in Lviv region. The section is composed of sedimentary formations of Yamna (Paleocene) Manyava, Vytrvysya, Popeli and Bystrytsya (Eocene) Formations and Lower Menilite Sub-Formation (Oligocene). These rocks are overlain with angular disagreement by a complex of Lower Miocene molasses, represented by salt-bearing clay deposits of the Vorotyscha Formation, containing numerous olistolithes of the Menilite rocks. The upper parts of Eocene sediments are represented by greenish-grey non-calcareous claystones with layers (2–5cm) of grey mudstones of the Bystrytsya Formation. The thickness of this suite in the Boryslav section is relatively small (up to 20 m) as here deposits are facially replaced by a clay-marl layer enriched by the fragments of exotic rocks. In the work (Vialov et al., 1988) these layers are known as the rock of the Popeli Formation. At the top of Eocene deposits there are traced light grey globigerina marls of the Sheshory horizon, alternating with dark grey claystones, grey and dark grey medium to fine-grained sandstones and mudstones. The black and brown-black non-calcareous shales of the Menilite type with layers of fine-grained sandstones and silicified marls are deposited above. These rocks form the Rybnytsya horizon, or «under-»rohovyk» («hornfels»).
horizon the base of which is considered to be a boundary between the sediments of Eocene and of Oligocene. Up the outcrop, the Menilite deposits are presented by silicites (phthanites and calcareous cherts) of the lower siliceous horizon (about 5 m). The outcrops of this horizon are clearly distinguished in the relief forming 2 m high «Boryslavskyy» waterfall and several small ones in the riverbed. Up the section, cherts are changed by black shales with layers of sandstones and mudstones and large lens-like carbonate concretions (Fig. 6).

The way from Boryslav to the village of Maidan firstly goes over a small ridge of the Skolivski Beskydy to the resort village of Skhidnytsia, which is also an interesting site for geological tourism. It is known primarily for its healing mineral waters. Here, in the Skhidnychanka river valley, the Stryi left tributary, there are numerous outcrops of black and dark grey clay, siliceous-clay and sandy rocks of the Menilite suite. However, the Eocene and Oligocene deposits boundary is outcropped here very poorly. The Skhidnytsya mineral water deposit had been discovered in 1958, and its exploration and commissioning continued till 1975. Based on the last one, an all-Ukrainian balneological resort named after Omelyan Stotsky works, the discoverer of the Skhidnytsya deposits of mineral waters of the «Naftusya» type. Catching sites for a tourist in Skhidnychanka are mineral water springs, a pump room, the St. Panteleimon Park with historical oil extraction exhibits, and the Omelyan Stotsky museum.

The further way to the village of Maidan goes via local roads. The first marking point is the Skhidnychanka river, then Novyi Kropyvnyk village, a road bridge across the Stryi river and, further, Rybnik village, the Rybnik river valley, the right tributary of Stryi. The area here is attractive thanks to the picturesque landscapes (Fig. 7).

Therefore, tourist excursions for holidaymakers, staying at Skhidnychanka sanatoria, are regularly held here.
to this interesting part of the Carpathian Mountains from Lviv by public transport, it’s necessary to take Lviv-Drohobych bus starting from bus station No 8 and then take a bus to Maidan village in Drohobych.

A large outcrop the Lower Menilite Sub-Formation rocks is observed on the banks of the Rybnik River, upstream its junction with the Maidan River (Parashka skyba). The closest settlement is Maidan village. It is possible to approach the outcrop via local road leading from Skhidnytsia village to Sambir-Turka-Uzhgorod highway. Among the Upper Eocene deposits, which underlie the Oligocene thickness, there is a thin unit of globigerina marls that stratigraphically correspond to the Sheshory horizon. The silicites of the lower siliceous horizon (5 m) are located above. The majority of the Lower Menilite deposits (visible power up to 100 m) is represented by typical black shales («menilite shales»), among which there are thin (10–40 cm) sandstone annunciators (Fig. 8).

In addition to the described outcrop, considered by us as a site for geological tourism, Maidan village is known for other attractions that may be of tourists’ interest. In Maidan there is a wooden church of the Dormition of the Mother of God, built in 1939, and the oldest blast furnace at the Skolivski Beskydy foot, near the Opir river, which flows into the Stryi river (Fig. 9). Parashka mountain (1270 m), the highest region in Lviv, rises above the Stryi river. (1268.5 m) – one of the highest region in Lviv.

The border between the Eocene and Oligocene deposits can be seen also in outcrops on the right bank of the Opir river, in the vicinity of Verkhne Synyovydne. Here rocks of the Bystrytsya Formation upper part, Sheshory, Rybnky and lower siliceous horizons come to the surface. The village is located on the second terrace of the Opir River. The Eocene-Oligocene section on the river steep right bank is clearly visible from the village. This outcrop is located opposite to a field camp of the Geological Department of Lviv I. Franko National University, where students have educational practices. In 60–80s of the 20th century there was a research laboratory of the IGGCM NAS of Ukraine located, which studied the possibility to use bituminous rocks of the Menilite Formation for asphalt production, filling compounds for concrete, additives for cement and other purposes.

Here, overlie rocks of the Sheshory horizon located at the top part of the Oriv skyba Eocene sediments.
They are presented by light grey marls (up to 0.5 m) with inter-layers of dark grey to black claystones. The Oligocene rocks overlie deposits of the Sheshory horizon. The Oligocene deposits, namely «under-rohovyk» («hornfels») horizon rocks (3 m) of Menilite type, are represented by black shales with inter-layers of sandstones. The lower siliceous horizon of the Menilite Formation (5 m) is traced in the section above and it is composed mainly of phthanites. They also were found in the «under-rohovyk» («hornfels») horizon in the form of thin (5 cm) layers. The siliceous horizon is the sequence of phthanites of massive texture. They contain block-like concretions of calcareous cherts (up to 0.5 m). Up the outcrop, the rocks are typical for the Menilite Formation and are represented by black bituminous, often silicified, shales (Fig. 10).

Fig. 10. Outcrop of Late Eocene and Oligocene deposits, Verkhnye Syniovydne, r. Opir (photos I. Popp): A – general view of the outcrop of the Upper Eocene Bystrytsya Formation deposits at the right steep bank of r. Opir; B – outcrop of the calcareous mudstones and marls of the Popeli Formation at the river-bed of r. Opir; C – outcrop of the contact of siliceous-clayey rocks of Rybnytsya (under-chert) horizon (1) with the layer of phthanites of the lower siliceous horizon of Oligocene (2) with the layer of phthanites of the lower siliceous horizon of Oligocene (2); D – general view of the outcrop of the Lower Menilite Sub-Formation deposits at the right steep bank of r(Opir); E – lens-like texture of calcareous cherts of the top part of siliceous horizon; F – layered and thin-layered texture of phthanites of the lower part of siliceous horizon.
Fig. 11. Opir river valley near Skole (photo I. Popp).

Fig. 12. Outcrop of Late Eocene and Oligocene deposits, Skole, r.Opir (photos I. Popp): A – clay-marl rocks of the Sheshory horizon of the Upper Eocene; B – outcrop of the lower siliceous horizon of the Lower Menilite Sub-Formation; C – contact of felsanites and calcareous cherts of the lower siliceous horizon; D – lens-like texture of calcareous cherts of the top part of siliceous horizon; E – general view of the outcrop of the Lower Menilite Sub-Formation deposits at the right steep bank of r. Opir.
Skole is the center of Skole district, Lviv region, located in the Ukrainian Carpathians in the Opir river valley, one of the historical centres of Boykivshchyna (city of Stryj district of Lviv region). Skole is attractive with its landscapes. The town is located in a basin, that is, it is surrounded by high mountains from all sides. That’s why it’s incredibly beautiful here any time of a year. A dense river network formed by the Stryi and Opir tributaries makes this area particularly attractive for summer tourism (Fig. 11). Skole is located in the middle of the Skolivski Beskydy National Park. The town’s name of the city gave the name of the National Park as well as the name of the rock mass, i.e. Skolivski Beskydy. Skole is a starting point for many tourist routes within the National Park. In particular, here labelled tourist routes to Lopata and Parashka mountains start, to waterfalls on the Kamyanka River, to the Svyatoslav mountain tract.

Within the town’s administrative boundaries and its suburbs minerals are represented mainly by building stones and mineral water sources. The earliest reference on the Carpathian iron ore (spherosiderites) from the outskirts of Skole (the Pavliv stream) dates back to 1472. The first industrial sandstone quarry was founded in 1887 in Kolodka, the northern outskirts of the town. Shortly thereafter people started to take sandstone and rock debris in Svyatoslav (Svyatoslav quarry) being the part of the Stryi suite (the Upper Cretaceous). This quarry has still being operated.

In Skole vicinity, the Opir river breaks through the subdued Skolivski Beskydy ridges, forming a terraced basin in relatively soft Eocene and Oligocene flysch deposits. At the same time, the Opir second and third terraces, on which the town actually is located, reaches the maximum development. The Palaeogene section is represented by the rocks of the Yamna (Paleocene), Maniava, Vygoda, Bystrytsia (Eocene) and Menilite (Oligocene) Formations. The Lower Menilite and Lopianetska sub-suites stand out among the last two. In the Eocene deposits upper part, the greenish terrigenous-clay layer of the Bystrytsia Formation is badly outcropped. The Sheshory horizon rocks (6 m) are represented by marl claystone and dense marls. The Rybnnyk horizon (2 m) is composed of black shale, marls, non-layered lush marl claystone. Above lie cherts of the lower siliceous horizon (about 20 m) of the Lower Menilite Sub-Formation, represented by phthanites and carbonaceaeous cherts (Fig. 12). Onward, they are replaced by black scratchy clay rocks of the Lower Menilite Sub-Formation, enriched with organic matter. This outcrop can be clearly seen from the right steep bank of the Opir River. On the left gently sloping bank there are individual exposures of clay-malmstone rocks of the Sheshory horizon and the Lower Oligocene cherts. These outcrops are easily reachable via road within the town, which is very convenient for geotourist excursions.

The lower part of lower siliceous horizon of the Lower Menilite Sub-Formation crops out along the Tysmenytsia river in the vicinity of Boryslov (Beregova skyba), the Opir river around Verkhne Synyovydne (Oriv skyba) and Skole (Skolivska skyba), the Oriava river around Korostiv (Parashka skyba), and basin of the Opir river around Tukhlya (Zelemysanka skyba) etc. It is represented by a pack of dark grey to black cherts (phthanites). The upper part is represented by light grey carbonate-siliceous rocks (calcereous cherts, siliceous marls) with layers and lenses of darker cherts (phthanites or phthanite-like calcereous cherts).

Let’s briefly dwell on the terminology of the siliceous rocks of the Menilite suite. There is certain inconsistency between regional geological traditions and generally accepted scientific terminology, which can also be told about to those tourists, interested in geology. The traditional term «rohovyk» («hornfels»), widely used in domestic and Polish geological literature, as well as in production, is incorrect from the petrographic point of view, as hornfels are rocks of contact metamorphism. The terms «siliceite» and «chert» is quite widely used for various lithological types siliceous rocks. They can be considered synonymous. L. G. Tkachuk (Tkachuk, 1955) and Ye. K. Lazarenko, M. P. Gabinet, O. P. Slyvko (Lazarenko et al, 1962) use the term «chalcedonolites», i.e. cryptobiogenic cherts, composed of chaledony and quartz of Menilite Formation. In the monograph of M. P. Gabinet (Gabinet, 1985) and in our works (Popp, 1995, Popp, Senkovsky, 1996, 2003, Popp et al, 2004a, b, Senkovsky, Popp, 2010, Senkovsky et al, 2012) the term «phthanites», i.e. jade-lake dark siliceites with admixed scattered organic matter. We use the term «limy siliceites» to mark cryptobiogenic siliceites with admixed carbonate material, which form the upper part of the lower siliceous horizon of the Menilite Formation.

Discussion. The global and regional events at the Eocene and Oligocene boundary.

When geologists study conditions of rocks occurrence and their material composition, they set the goal, firstly, to reconstruct events of the geological past, and secondly, to develop certain search criteria for various types of minerals, including oil and gas. Sediment deposits encode information on events occurred millions years ago, which geologist should be able to read. Such information is very interesting both for geologists and for those who are interested in geology as amateurs. For instance, geological studies can show changes in paleogeographic and paleoclimatological situation, which led to environmental crises and mass extinction of various groups of organisms. Moreover, some lithological types of sediment deposits, in
particular siliceous oozes, have undergone significant post-sedimentation transformations over millions of years. Therefore, a geologist studies rocks, the origin of which is sometimes very difficult to define. The problem of siliceous rocks origin (silicites) of the Cretaceous-Palaeogene flysch in the Carpathians (biogenic, chemogenic or volcanic?) is practically debatable. When during geological excursions tourists see these outcrops clearly expressed in the relief, it is possible to tell about the points of view on their origin.

Sedimentary deposits of the Late Eocene – early Oligocene age of the Carpathian flysch are evidences of global environmental catastrophe. This catastrophe was the first mass extinction of marine and terrestrial organisms immediately after the extinction of dinosaurs and other giant reptiles at the Cretaceous-Palaeogene boundary («K-T boundary»). The «K-T boundary» in the sedimentary complex of the Ukrainian Carpathians is lithologically hidden in the sequence of the Upper Stryi sub-suite (Maastricht – Lower Palaeocene), formed as a result of intensive terrigenous sedimentation during lowering of the sea level and represents a typical flysch. The «K-T boundary» in these sediments can be seen very arbitrarily. The Eocene-Oligocene boundary events, by contrast, are clearly reflected in a stratigraphic sequence of sedimentary layers, formed during the sea-level rise and weakening of terrigenous sedimentation rates in the Carpathian basin.


Fig. 13. Paleooceanographic situation in Late Eocene – Early Oligocene (35 million ago): a – a planetary scale; b – in the western part of the Tethys Ocean after (Zonnenshain, 1987). 1 – land; 2 – shelf (continental crust); 3 – continental slope (thin continental crust); 4 – deep basins with the oceanic crust. I – Europe; II – Africa; III – Pannonian micro-continent; IV – Carpathian basin of Paratethys; V – Black Sea-Caucasian basin of Paratethys; VI – Mediterranean Sea; VII – Ionian Sea; VIII – Atlantic Ocean.
At the Eocene and Oligocene boundary and then during the Oligocene the World Ocean demonstrated a series of events that ultimately led to the transformation of a global system of ocean waters circulation from the Cretaceous-Eocene, marked with uniformly warm climate throughout the planet, to contemporary with more contrast climate and distinct climatic zones. Due to opening the Atlantic, the East Tethys had almost closed till the early Oligocene, drastically limiting western flows towards the Tethys Sea. Between Australia and South America and Antarctica formed straits, which led to the emergence of circular currents around Antarctica and its subsequent thermal isolation (Fischer, 1984, Kennet, 1982) (Fig. 13A). Continental blocks separated the vast Paratethys Sea with deep-sea basins isolated by several shallow seas in the Western Tethys: the Black Sea-Caucasus and the Carpathian (Popov, et al., 2009, Zonnenshin et al., 1987) (Fig. 13B).

Fauna and flora of the Paratethys northern coast in the late Eocene indicate subtropical conditions with average annual temperatures of 15–20ºC, cold month – 6–13ºC, warm month – 15–25ºC. Later, in the early Oligocene the signs of cooling gradually developed, the diversity of marine fauna reduced, the role of deciduous and coniferous terrestrial vegetation greatly increased and climate aridisation intensified. The average annual temperatures diminished by 4–6ºC (Popov, et al., 2009, Ushakov, Yasamanov, 1984).

In the late Eocene – early Oligocene changes in marine and terrestrial biota occurred, explained by some researchers (Alekseiev, 2000, Fischer, 1984) as the Eocene – Oligocene minor mass extinction. This biotic crisis began from marine biocenoses at the Eocene and Oligocene boundary, lasted over millions of years and encircled ground biocenoses in the early Oligocene. First of all, it was caused by the global climate change due to the movement of lithospheric plates and influenced the nature of ocean circulation (Jenkins, 1974, Kennet, 1982). Though, some researchers (Keller, 1986, Varenschov, 2007) assume that at that time an impact event could happen (Earth’s collision with a comet or asteroid). This opinion is not shared by P. N. Pearson et al. (Pearson, et al. 2008), who notes that none of the samples of hemipelagial deposits of Tanzania studied by them were not found microtectites or other evidence of an impact event at the turn of Eocene and Oligocene. These authors believe that the Eocene-Oligocene biotic crisis occurred step by step. This biological crisis leads to profound changes in the global climate and marks the end of a long period of predominantly «greenhouse» conditions on the Earth, which lasted since the Mesozoic. These events contrast with sudden and catastrophic mass extinctions, such as the end of the Cretaceous.

The most recent published research results (Elsworth, et al., 2017) testify that cooling of Antarctica and global climate change at the Eocene and Oligocene boundary were the result of two factors about 35 million years ago. Originally, the Drake Strait, which divides Antarctica and South America, became deeper and wider, which increased mixing of water in the polar latitudes of the Pacific and Atlantic oceans. Warm currents, such as the Gulf Stream, began moving faster towards the north, providing accelerated cooling of Antarctica. All this allowed for emerging of the second factor: reduction the atmospheric carbon dioxide level, which started to reduce since the beginning of the Cenozoic, more than 60 million years ago. However, changes in ocean currents accelerated this process. It began raining much more often, causing washing out carbon dioxide from the air, which, interacting with rocks, penetrated into them. Accordingly, its warming «greenhouse» effect also went down.

According to (Alekseiev, 2000, Foster, 1974, Jenkins, 1974, Kennet, 1978, 1982) planktonic foraminifera (Foraminifera), coccolithophorida (Coccolithophorales), silicophlagellata (Silicophlagellatæae) and other groups of pelagic organisms suffered as species and partly as genera. The replacement of planktonic foraminifera systems from the late Eocene, characterized by the diverse species and complex forms, such as Globigerapsis and Hankenina, to the Oligocene simple forms Globigerina and Globigiralia is fixed. Also, sudden changes at the Eocene and Oligocene boundary suffered the Antarctic diatom complexes (Diatoméae). At genus level a significant extinction of marine benthos is detected. For example, in South Australia warm-water sea urchins (Echinoidea) were changed by the cold-water ones (Foster, 1974, Kennet, 1982).

Change of warm-water plankton organisms for those accustomed to live in cold seas can be illustrated by the results of study of calcareous and siliceous rocks of the Eocene-Oligocene deposits in the Ukrainian Carpathians. The Sheshory horizon marls are composed of cryptocrystalline clay-carbonate matter with numerous remains of warm-water forms of planctonic foraminifera (single-celled animals with calcareous skeleton) from a group of globigerina (Globigerinida) sized up to 0.1 mm(Fig. 14). The number and size of these organisms significantly reduced in the rocks of Rybnik horizon. No their traces are found in siliceous formations, which is the evidence of changing the environmental conditions in marine basin. In the Menilite Formation siliceous rocks there are skeletal remnants of siliceous planktonic organisms (mainly diatoms) observed, accustomed to live in moderate and cold climates.
The importance of the problem considered in this article is confirmed by the fact that in 1980 the project No 174 «Geological events on the border of the Eocene and Oligocene» was included in the International Geological Correlation Program (IGCP). According to the results of these studies, the boundary between the Eocene and Oligocene on a global scale is drawn at the level corresponding to the extinction of Hantkeninidae, in the Massignano area near Ancona in Italy (Silva, Jenkins, 1993). A group of scientists who studied the contact zone of Eocene and Oligocene deposits in the Ukrainian Carpathians and adjacent regions took part in the development of the project topic No 174. According to these studies, there was a degradation of benthic and even planktonic foraminifera, which indicates a sharp deterioration of organic living conditions in the Carpathian Basin between the Eocene and Oligocene. Hydrogen sulfide contamination appears in its deep-water part in the early Oligocene in the Carpathian Basin (Vyalov et al., 1987). In the Ukrainian Carpathians, the boundary of the Eocene and Oligocene is distinguished by the contact of the Globigerina corpulenta zone (the roof of the Bystrytsya Formation—the Sheshora horizon) and the layers of Globigerina vialovi (the sole of the Menilite Formation), which is reflected in continuous sections of the Skyba and Dukla zones (Gruzman, 1987). In the zone of Globigerina corpulenta (Sheshora horizon) the zone of Coccolithus subdistichus is distinguished by nanoplankton, above the zone of Kisselovia clathrata angulosa (Andreeva-Grigorovich, 1987, Dabagyan, 1987) is distinguished in the lower Menilite deposits. There is also a change in the complexes of foraminifers on the border of the Eocene and Oligocene in southern Ukraine, Romania, Hungary, western and northern Slovakia, in the Polish Carpathians (Kraeva, Maslun, 1987).

Climate cooling at the turn of the Late Eocene – Early Oligocene has been established by the results of various geochemical studies, including the study of the isotopic composition of oxygen and carbon, in many regions of the world. Flysch deposits of the Polish Outer Carpathians (Olszewska, Szydło, 2017), carbonate deposits of Tanzania (Pearson, et al., 2008) and the Central Mediterranean (Cornacchia, et al., 2018), otoliths of mollusks of the coastal plain of the Gulf of Mexico (Ivany, et al., 2000), findings of tooth enamel of large, water-dependent, herbivorous terrestrial mammals of southwestern Europe (Kocsis et al., 2014), North American paleosoils (Sheldon, et al., 2002) were studied in this context.

From mammal (Mammalia) marine animals, which disappear from the fossil record at the Eocene and Oligocene boundary, separately should be noted primitive or ancient whales—arheocetes (Archaeoceti) (Kennet, 1982). Arheocetes of the late Eocene were already marine animals but still retained some relict signs of their land ancestors, in particular rudimentary lower limbs. The largest of them, representatives of the group of basilosauri (Basilosauridae) had an elongated body and were from 12–15 m to 20–25 m long. They did not have whale fat (whale-oil) and were adapted to live exclusively in warm tropical or subtropical climate. The name «basilosaurus» (Basilosaurus) means «king of lizards» and was given by mistake. Their remnants were first found by a paleontologist Harlan in Alabama (USA) in 1834 and who took them for a skeleton of a giant reptile. These paleontological findings were found in the Sahara, Europe, Pakistan and India. This means, that basilosauri lived in the late Eocene across the whole Tethys, where the warm climate prevailed. In Ukraine, the first arheocetes were found in the 19th century near Chyhyryn. Throughout the 20th century,
such fossils were found in Kirovohrad, Cherkassy and Luhansk regions and in suburbs of Kyiv. P. Goldin et al., described these samples in detail and were able to identify the previously unknown genus and species Basiloritus uheni. Researchers consider that the geographical discoveries and limited distribution of the whales opens a possibility to use them in biostratigraphic schemes (Goldin et al., 2012, 2013, 2014). The archeocetes distribution area in the late Eocene was a warm shallow sea coast of the Tethys. Most likely that they did not swim in into deep basins, particularly in the Carpathian sea. The toothed whale (Odontoceti) filled the ecological niche of archeocetes in the early Oligocene. Baleen whales (Mysticeti) appeared in the middle of the Oligocene. The most ancient remnants of these animals are known in marine sections of New Zealand (Kennet, 1982). The described changes per cetaceans (Cetacea) species and genera composition at the Eocene and Oligocene boundary is a clear sign that global climate began to cool. It should be noted that the modern research established the impact of lithospheric plates tectonics (drift of continents) on the climate change and the formation of migration routes of certain groups of animals, or the isolation of certain terrestrial biomes. Because of opening or closing of certain straits, the system of ocean circulation changed, which significantly affected the climate (Kennet, 1982). The impact of these processes on the evolution of organic world was quite noticeable, though stretched in time for the hundreds of thousands and millions of years. Even more catastrophic changes occurred in the organic world as a result of impact events, such as at the Cretaceous-Palaeogene boundary, or a sharp strengthening of volcanic activity, such as at the Permian-Triassic boundary (Aleksieiev, 2000).

The biotic crisis of the Eocene-Oligocene was the first event of such type after the extinction on the boundary of Mesozoic and Cenozoic. Nevertheless, unlike the latter it did not lead to the deep qualitative re-organisation of higher vertebrates fauna. Due to the global catastrophe in the late Cretaceous period, there was a dramatic replacement of the kingdom of dinosaurs, pterosaurs and giant marine reptiles (ichthyosaurs, plesiosaurs, mosasaurs) for the kingdom of mammals and birds. Obviously, the crucial significance in this case was played by an impact event. The Eocene-Oligocene mass extinction was more stretched in time and took place in two stages. At the Eocene and Oligocene boundary genera and species of different groups of marine organisms (phytoplankton and zooplankton, benthos, marine mammals) were re-structured. In the early Oligocene some groups of land mammals experienced extinction. Such biotic crisis was caused by the global climate change. It began in the Antarctic region and spread to the north, first in marine, and then in terrestrial ecosystems. The biotic crisis of the Eocene-Oligocene was the first event of such type after the extinction on the boundary of Mesozoic and Cenozoic. Nevertheless, unlike the last one it did not lead to the deep qualitative re-organisation of higher vertebrates fauna. Due to the global catastrophe in the late Cretaceous period, there was a dramatic replacement of the kingdom of dinosaurs, pterosaurs and giant marine reptiles (ichthyosaurs, plesiosaurs, mosasaurs) for the kingdom of mammals and birds. Obviously, the crucial significance in this case was played by an impact event. The Eocene-Oligocene mass extinction was more stretched in time and took place in two stages. At the Eocene and Oligocene boundary genera and species of different groups of marine organisms (phytoplankton and zooplankton, benthos, marine mammals) were re-structured. In the early Oligocene some groups of land mammals experienced extinction. Such biotic crisis was caused by the global climate change. It began in the Antarctic region and spread to the north, first in marine, and then in terrestrial ecosystems. The biotic crisis of the Eocene-Oligocene was the first event of such type after the extinction on the boundary of Mesozoic and Cenozoic. Nevertheless, unlike the last one it did not lead to the deep qualitative re-organisation of higher vertebrates fauna. Due to the global catastrophe in the late Cretaceous period, there was a dramatic replacement of the kingdom of dinosaurs, pterosaurs and giant marine reptiles (ichthyosaurs, plesiosaurs, mosasaurs) for the kingdom of mammals and birds. Obviously, the crucial significance in this case was played by an impact event. The Eocene-Oligocene mass extinction was more stretched in time and took place in two stages. At the Eocene and Oligocene boundary genera and species of different groups of marine organisms (phytoplankton and zooplankton, benthos, marine mammals) were re-structured. In the early Oligocene some groups of land mammals experienced extinction. Such biotic crisis was caused by the global climate change. It began in the Antarctic region and spread to the north, first in marine, and then in terrestrial ecosystems.

**Origin of cherts**

Siliceous rocks (cherts) are distributed within the sedimentary layers of both plain platform and folded mountainous areas. The high solidity is a characteristic feature of cherts. There is a suggestion, that they were used as the first mineral resources, extracted by a man. Primitive people used cherts (silicites) for making stone tools. The concretion cherts from the Volya-Podillya carbonate sequence are the most suitable for such purposes. If the Carpathian Oligocene cherts (silicites) were used by people of the Stone Age, most likely, it was not a common practice. These rocks are of layered texture, caused by the uneven distribution of organic, clay or carbonate components. They are easy to be split along the sheeting planes and less suitable for making stone tools.
The development of geological sciences, especially sedimentology and lithology, led to the rise of the following question: how sedimentary rocks, which sometimes contain more than 90% of authigenic SiO₂ (chalcedony and microcrystalline quartz), formed?

There are different points of view on the origin of the Menilite Formation cherts. Within the Menilite Formation there are three horizons of these rocks, i.e. the lower siliceous of the Lower Menilite Sub-Formation, thin siliceous layers at the top of the Lower Menilite Sub-Formation, the upper siliceous of the Upper Menilite Sub-Formation. Major challenge is to establish the source of silica that form siliceous oozes (migration from the continent or volcanic processes), and its mode of deposition (biogenic, chemogenic).

Biogenic origin of such cherts as diatomites, radiolarites, spongolites that have a clearly expressed biomorphic structure does not cause doubts. However, in the folded Carpathians thecryptogenic quartz-chalcedony cherts are more common, affected by considerable post-sedimentary changes. Therefore, the origin of such siliceous rocks is debatable enough.

The main lithological type of the Menilite Formation cherts is phthanites. These are siliceous rocks mixed with scattered organic matter, composed of microcrystalline quartz, among which fan-shaped aggregates of fibrous chalcedony and rare skeletal remains of organisms with siliceous skeleton (diatoms, radiolarians) occur. It is very difficult to determine the initial siliceous sediment in thin-sections.

The origin of these siliceous rocks has caused concern in the pre-war and post-war period among Polish, Romanian and Czech geologists. There were hypotheses about their formation as a result of deposition of biogenic siliceous oozes or silicification of carbonate rocks. The development of their views on the subject of silica deposition in the Carpathian sedimentary basin is very well shown in the work of E. K. Lazarenko, M. P. Habinet, A. P. Slyvko (Lazarenko et al 1962). In particular, in 1931 the Romanian geologist M. G. Filipescu expressed an opinion on the rapid development of diatoms in the Carpathian Basin. A. Gaweł in 1951 argued that silica was supplied by river streams in the Menilite basin and reprocessed by organisms with siliceous function. According to Cz. Kuźniarin 1952, diatoms migrated into the Menilite basin with currents from the North Sea. The appearance of siliceous rock horizons (sherts) in Lower Menilite sediments is associated with the cooling of the climate in the early Oligocene (Olszewska, Szydło, 2017).

M. P. Gabinet (1985) links the development of diatom flora and biogenic silica deposition in the Carpathian Basin with volcanic and post-volcanic (hydrothermal) processes. In some of our works (Popp, 1995) the correlation of biogenic silica deposition with volcanic and post-volcanic activity is also made.

Some researchers have suggested that cherts formed due to chemogenic deposition of SiO₂ (Majewski, 1994) or silicification of volcanic formations (Reyfman, 1971, 1980).

We (Popp et al, 2004⁴, Senkovsky et al, 2010, 2012) believe that the main reason for accumulation of siliceous sediments in sedimentary basin of the continental margin of the Carpathian segment of the Paratethys in the Oligocene were extensive flashes of zoo and phytoplankton with a siliceous skeleton associated with periodic coastal upwelling (uplift of cold ocean waters, rich the nutrients (siliceous, phosphorus, microelements) to the photosynthesis zone). We consider siliceous layered chalcedonolithes, phthanites and calcareous cherts as a product of deep post-sedimentary transformation of biogenic siliceous sediments mainly of diatom and radiolarian composition. Structural and texture features and material composition the Oligocene cherts in the Ukrainian Carpathians show that formation of biogenic siliceous sediments occurred in a severe deficiency of oxygen. Geochemical processes, involving organic matter, contributed to the dissolution of skeletal remains of siliceous organisms and transformation of opal-like forms of silica into chalcedony and cryptocrystalline quartz. We consider the studied siliceous rocks to be indicators of oceanic anoxic events (regional phase OAE-4, defined by (Senkovsky et al, 2004, 2012)) when there were conditions to accumulate large amounts of organic matter in marine sediments. In the work (Popp et al, 2004⁴) we justify the genetic relationship between biogenic silica deposition and processes of organic matter sedimentation. Silica-clay depositions of the Menilite Formation, enriched with an admixedtured organic matter, are considered as an oil-source layer.

Conclusions

Hence, an interest to the horizons of carbonate and siliceous rocks at the Eocene and Oligocene deposits boundary in the Ukrainian Carpathians as the site for geological tourism is supported by the fact that:

• outcrops of (silicites) are clearly expressed in the relief and create small waterfalls and rapids on rivers, rocky cliffs on mountain slopes and can be considered as natural monuments (or geological monuments);
• at the Eocene and Oligocene boundary there were series of interesting paleooceanographic, paleoclimatic and sedimentological events of global and regional importance;
• the problem of the Menilite Formation cherts (silicites) origin was and has remained rather controversial.

Authors of the article believe that these rocks are the product of sedimentation of biogenic siliceous oozes and their post-sedimentary transformation.
References


