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MINERAL COMPOSITION AND MICROSTRUCTURE OF FLINTS OF SKYBA NAPPE MENILITE FORMATION OF UKRAINIAN CARPATHIANS

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On the basis of X-ray and electron microscopic analyzes the mineral composition and microstructures of gray, brown and black flints in menilite formation of Skyba nappe of Ukrainian Carpathians have been studied.

It has been found that brown flints mainly consist of lightly crystallized chalcedony and chalcedony with significant amount of calcite, the gray and black flints consist of chalcedony with arranged structure similar to the quartz. The lasts consist of rests of radiolarians and coccoliths. Presence of microfauna in flints confirms the biogenic origin of ones.

Key words: Ukrainian Carpathians, menilite formation, flints, chalcedony, microfauna, biogenic origin.

The flints (silicides) are spread in many structural-facial zones of Ukrainian Carpathians. The results of their study were published in many papers and monographs [2, 3–8] and others. In the Skypa nappe of Carpathians the flints are most spread in menilite formation. Here they lie as the basis horizons (4–12 m) and roof (0.5–1.0 m) of low-menilite nappe and in base of upper-menilite formation (4–6 m) [3]. Their mineral composition and conditions of formation was little studied. In connection of student practice of geological mapping around near Hrebeniv and Verkhnye-Synyevydne villages the necessity of its detailed study has arisen. To this end, the samples of low-menilite (sp. 3, 5) and upper-menilite (sp. 4, 7) sub-nappes were picked up and mineral composition and microstructure on the basis of X-ray and electron microscopic analysis were carried out.

The intense reflexes 4.25; 3.34; 2.45; 2.28; 2.23 Å and others are observed on diffractograms of silicides (Fig.1) They may belong to both the quartz and its hidden crystalline variant – chalcedony.

According to M. Yakovlyeva and others. [11] there is a difference in the intensity of their reflexes. To diagnose these differences, they recommend to use reflexes 2.45, 2.28 and 2.23 Å. X-rays reflex of chalcedony 2.45 Å is always weaker than 2.28 Å and only in rare cases they are equal, whereas on quartz radiographs the reflex 2.45 Å is stronger than 2.28 Å.

The weakest among them is the reflex 2.23 Å. In Chalcedon it is poorly expressed or significantly weaker than 2.28 Å (its height is less than half the height of reflex 2.28 Å). For quartz the difference in intensity reflexes of 2.23 and 2.28 Å, of course, smaller (2.23 Å peak height is not less, and preferably larger than half height of 2.28 Å).

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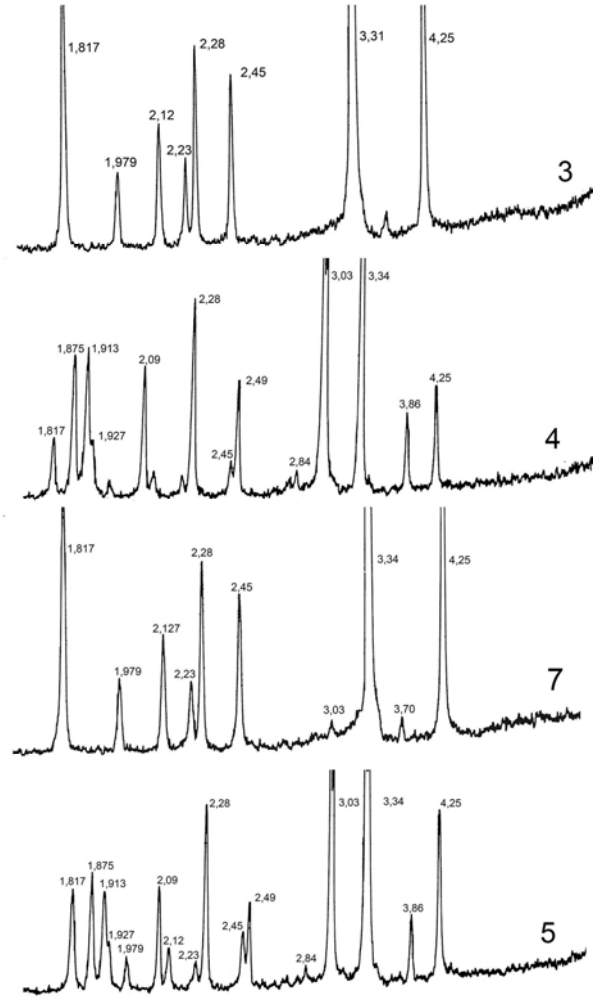

Fig. 1. The diffractograms of flints of Skyba nappe menilite formation of Ukrainian Carpathians. The flints: *3* – black, *5* – Brown, board of r. Oryava river, near Korostiv village; *4* – Brown, *7* – light gray, oxbow of r. Opir near Verkhnye-Synyovydne village.

In diffractograms of brown flints (sp. 4, 5) reflexes intensity ratio of 2.45:2.28 Å is less than one and varies between 0.20–0.32, while the flints of light gray and black (sp. 3, 7) it is much larger and is 0.83–0.86. In brown sample the intensity ratio of reflexes 2.23:2.28Å is also very small (0.12–0.16), and others it is much higher (0.37–0.38).

Besides, brown flint contains many calcite (3.86; 3.03; 2.49 Å), whereas in light gray and black ones it is absent (Fig. 1).

According to these data, brown flints are represented by slightly-crystallized chalcedony and light gray and black ones by the arranged structure similar to quartz.

Important information on structural features and conditions of formation of flints of menilite formation of Skyba nappe of Ukrainian Carpathians was obtained as a result of studying with scanning electron microscope JEOL-T220A. The identification of residues of microorganisms is of great importance.

Among researchers, there are two points of view on the origin of flints in sediment: chemical and biogenic ones [9]. Concerning the possibility of chemical origin of flint, it should be noted that the amount of silicon in sea water is very low – 3 mg/l. For chemical deposition of silica it is necessary that its concentration in the water was at least 100 mg/l. Therefore the silica could be chemically formed in marine sediments and in deposits of sediments only if significant amount of hydrothermal solutions comes in sedimentary basins and in the rock strata through con-sedimentary fractures and faults. In this case, the remains of nanoplankton in flint of chemical origin are missed.

In modern sediments of seas and oceans the organisms of diatoms, radiolarians, sponges and their remains in flints of sedimentary rocks can be found [1, 10, 12]. In the process of transformation of bottom deposits into sediment rocks, at the stage of early diagenesis, their structure is being recrystallized and destructed. These processes are further enhanced in the late stages of diagenesis and catagenesis. Despite this, the remains of their bodies sometimes are preserved. The discovery of such fossils of microorganisms in flint confirms that they have a biogenic origin.

It should be noted that the nodules and flint horizons in sedimentary rocks, including a menilite formation of Skybova nappe of Ukrainian Carpathians, are not distributed across whole flysch section, but only in individual intervals. This is because the significant development of silicon organisms occurred in the case of high silicon content in sea water, which could come as pyroclastic material, mainly ash and hydrothermal ones. Silicon organisms are able to concentrate the silica from environment in hundreds and thousands times as much for its own needs. This is unique feature of living organisms.

In this regard, the study of microstructures flints is of considerable interest. As a result of electron microscopic study of flints from menilite formation it has been found that their internal structure is mainly granular and globular one (Fig. 2).

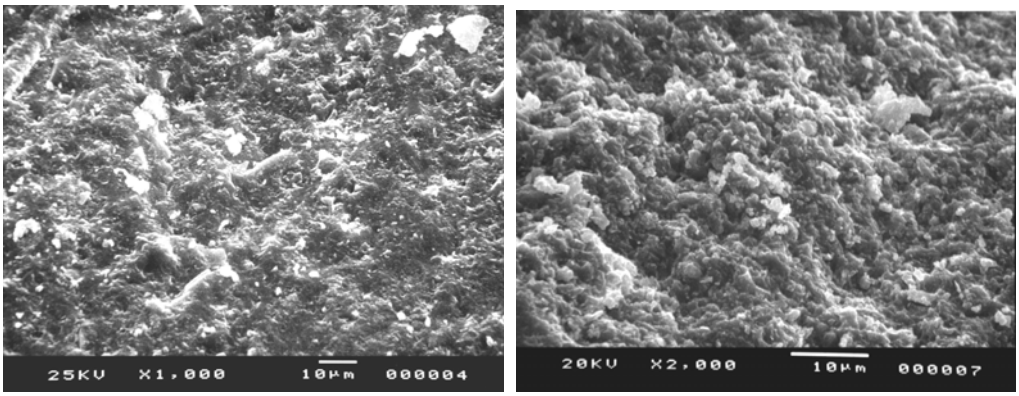

Fig. 2. Microstructure of brown (sp. 4) and light gray (sp. 7) flints.

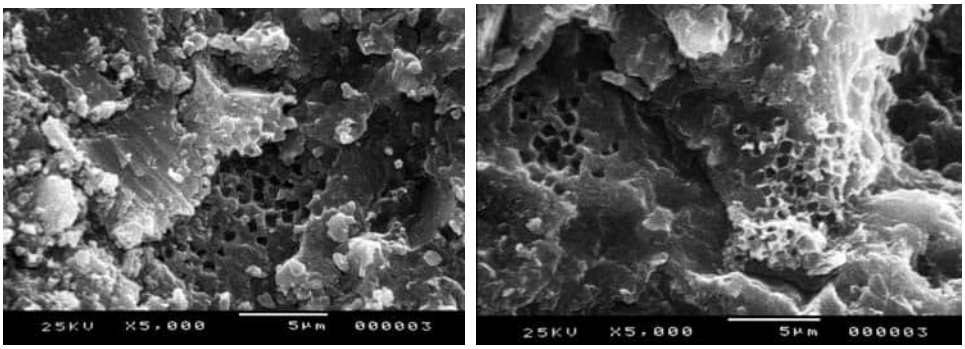

Fig. 3. The remains of radiolarians in black flint.

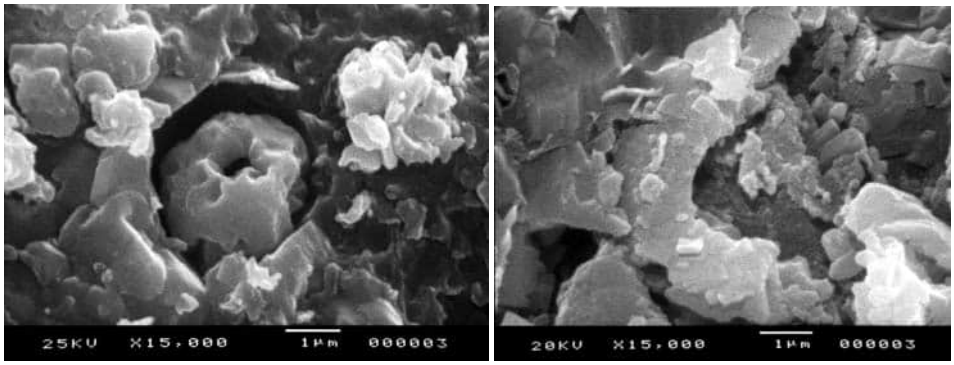

Fig. 4. Remains of coccoliths in black flint.

The identification of residues of radiolarians (Fig. 3) and coccoliths (Fig. 4) is of important significance. It is observed also the traces of dissolution of coccoliths. A lot coccoliths is in light gray flint (Fig. 5). The crystallomorphic structure is very clearly expressed in relief of brown flints. Here the well-faceted microcrystals of calcite and somewhere quartz are observed (Fig. 6).

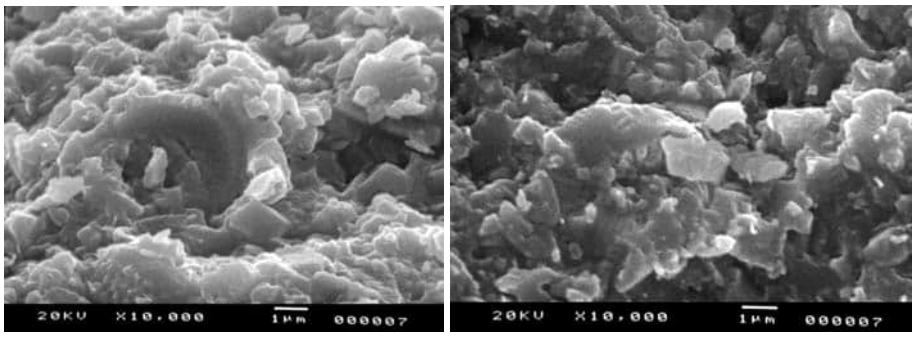

Fig. 5. Remains of coccoliths in light grey flint.

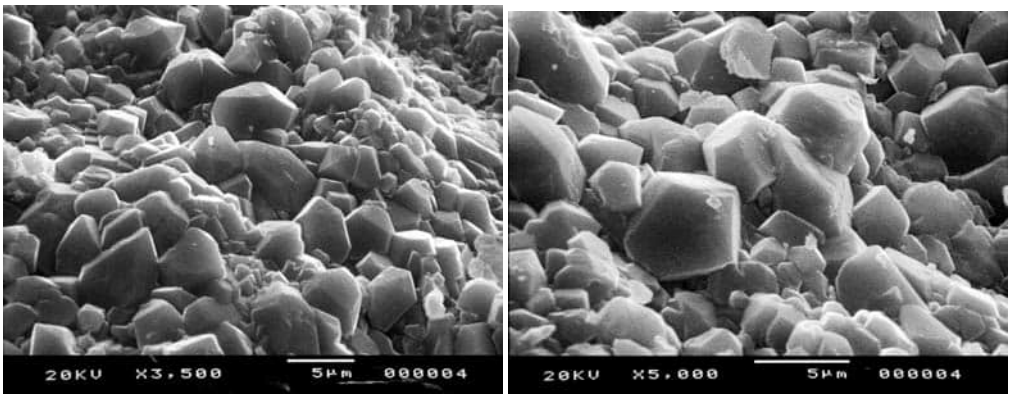

Fig. 6. Crystallomorphic microstructure of brown flint.

So, in menilite formation of Skyba nappe of Ukrainian Carpathian the light gray, brown and black flints are present. They differ in mineral composition and microstructure. Brown flint is presented by slightly crystallized chalcedony with high content of calcite in the form of well-observed microcrystals. Light gray and black flints are also represented by chalcedony with well ordered structure close to quartz. They contain the remains of radiolarians and coccoliths. The presence of micro fauna in flints of menilite formation confirms their biogenic origin.

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МІНЕРАЛЬНИЙ СКЛАД І МІКРОСТРУКТУРА КРЕМЕНІВ МЕНІЛІТОВОЇ СВІТИ СКИБОВОЇ ЗОНИ УКРАЇНСЬКИХ КАРПАТ

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Вивчено мінеральний склад і мікроструктури світло-сірих, чорних і коричневих відмін кременів з менілітової світи Скибової зони Українських Карпат за даними дифрактометричного і сканувального електронно-мікроскопічного аналізів.

З'ясовано, що коричневі кремені представлені слабко окристалізованим халцедоном зі значним вмістом кальциту, а світло-сірі й чорні – халцедоном з упорядкованою структурою, близькою до кварцу. У світло-сірих і чорних кременях виявлено залишки радіолярій і коколітів. Наявність у кременях мікроструктури засвідчує їхнє біогенне походження.

Ключові слова: Українські Карпати, менілітова світа, кремені, халцедон, мікрофауна, біогенне походження.