ISSN 2078-6220. Мінералогічний збірник. 2016. № 66. Випуск 2. С. 118–127
Mineralogical Review. 2016. N 66. Issue 2. P. 118–127

UDC 558.493.5.041:552.33(510)

PECULIARITIES OF DISTRIBUTION, COMPOSITION AND ORIGIN OF GLAUCOPHANE FROM DABIE-SHAN (CHINA)

V. Guliy[1], I. Poberezhska[1], O. Kovtun[2]

[1]*Ivan Franko National University of Lviv,*
4, Hrushevskyi St., 79005 Lviv, Ukraine
E-mail: vgul@ukr.net
[2]*Ukrainian State Geological Research Institute,*
78a, Avtozavodska St., 04114 Kyiv, Ukraine
E-mail: ukrdgri@ukrdgri.gov.ua

Peculiarities of distribution of glaucophane in the Precambrian rocks of the Dabie-Shan area (China) and its composition are described. Glaucophane is the main mineral of the Upper Proterozoic Mulanshan–Zhangbaking blue schist belt. Glaucophane is unevenly distributed in the leucocratic rocks of the belt, and in melanocratic units it is concentrated in glaucophane schists. Appearance of glaucophane is determined by primary composition of initial rocks. Chemical composition of glaucophane from the blue schists belts in different regions and from the Dabie-Shan region is similar, but with some local variations. Isotopic composition of C and O from the different types of carbonates is variable, but in general it indicates the absence of large-scale processes of recrystallization with participation of mobile CO_2. Main characteristics of investigated rocks and minerals are connected with initial composition of the rocks.

Key words: glaucophane, blue schists, high- and ultrahigh pressure, petrogenesis, isotopes of O and C, Upper Proterozoic, Dabie-Shan, China.

After the pioneer work of O. Leypunskiy [13] on pressure and temperature limits of stable phases of graphite–diamond transitions, petrologists regarded conditions of the upper mantle and lower Earth crust as suitable for formation of diamond from magmatic sources.

Similar pressure and temperature conditions have been supposed for mineral assemblages of the regional metamorphic rocks which include diamond-bearing varieties and specific diamond-bearing eclogite subfacie (eclogite facie in opinion of P. Eskola [10]) has been proposed for them. Beside of diamond, presence of coesite, glaucophane, rutile, lawsonite, cornerupine, kyanite etc. have been suggested as an indicator of high pressure regime under regional metamorphism for some large-scale folding structures and big areas within the Precambrian blocks. N. Dobretsov [4] generalized a great material on distribution of the Phanerozoic glaucophane-bearing rocks and established of the blue schists belts in association with eclogites. Among granulites of the Aldan Precambrian Shield, the Sutam subfacie of regional metamorphism with extremely pressure conditions has been determined after sapphirine finds [5].

This list of places with very specific conditions of regional metamorphism can be continued due to a great success of geologists during last decades in investigations of collision regimes with common high (HP) and ultrahigh pressure (UHP) tectonic structures. Among of them, the most famous structures are Dabie-Shan and Dabie-Sulu, China [18, 20, 23], the Western Gneiss region, Norway [6, 7, 15], the Precambrian Kokchetav massif, Kazakhstan [8, 16, 24] etc.

According to modern scheme of metamorphic rocks mineral facies, proposed by S. Bushmin and V. Glebovitsky [2], which is suitable to use for these structures and estimate relationships between their mineral associations, there are not clear evidences for dividing rich in diamond rocks varieties and without it. Similar situation there is for HP and UHP segments of the scheme [1], where can't be determine scale of diamonds enrichment of glaucophane- and kyanite-bearing rocks.

Paradoxical irregular appearance of unusual minerals which have commonly regarded as indicators of special pressure conditions lead us to conclusion about absent of pressure controlling factor for their formation. Most clear evidences for this conclusion can be obtain from analysis of diamond distribution in the rocks of the Kumdykol deposit and the Barchy diamond-bearing zone at the Kokchetav massif, Kazakhstan, as well as assemblages diamond with graphite, diamond locations in quartz, chlorite, sericite, feldspar, clinopyroxene etc. [8, 16, 24].

In addition to these facts we should note also about inclusions of carbonates, barite and ferro-oxydes in diamonds [9], and diamond inclusions in apatite [22] etc. in different rocks from other regions.

Taking into account suggestions on relationships of diamond enrichment and composition of diamond-bearing rocks in the Kumdykol deposit and the Barchy diamond-bearing zone [16] we attempted to determine the distribution, composition and origin of glaucophane in connection with composition variations of the host rocks in the Dabie-Shan area as the etalon of high pressure region.

Geological setting and main rocks types. The Dabie-Shan region of Hubei, Henan and Anhui Provinces and the Lianyungang area of Jiangsu Province (Fig. 1) is located on the south-eastern margin of the North China Platform [3, 23].

Geological structure of the Dabie-Shan is complicated due to a number of tectonic events since formation of the Archean up to modern time, when collision processes reworked and moved previously stable blocks.

Upper Archean gneisses-migmatites complex is the oldest. It is covered by the Lower Proterozoic Dawu–Susong–Lianyungang phosphate rocks and younger rocks of the Upper Proterozoic Mulanshan–Zhangbaking blue schists belt. Upper Proterozoic Sujiane–Foziling schists have sporadic distribution in the northern segments of the Dabie-Shan region [23].

The Upper Archean rocks are represented by tonalite-trondhjemite-granodiorite orthogneisses and banded iron ore formation [20, 23]; elongated bodies of eclogites have been described among them [3, 23]. Series of metasedimentary and volcano-sedimentary formations are typical for the Lower Proterozoic suite, which is rich in exotic combinations of the schists, gneisses, leucoleptenites, epidote amphibolites, marbles phosphate rocks with relic bedding. Blue schists, phyllite metamorphic sodium rich volcanic series are common components of the Upper Proterozoic sequences.

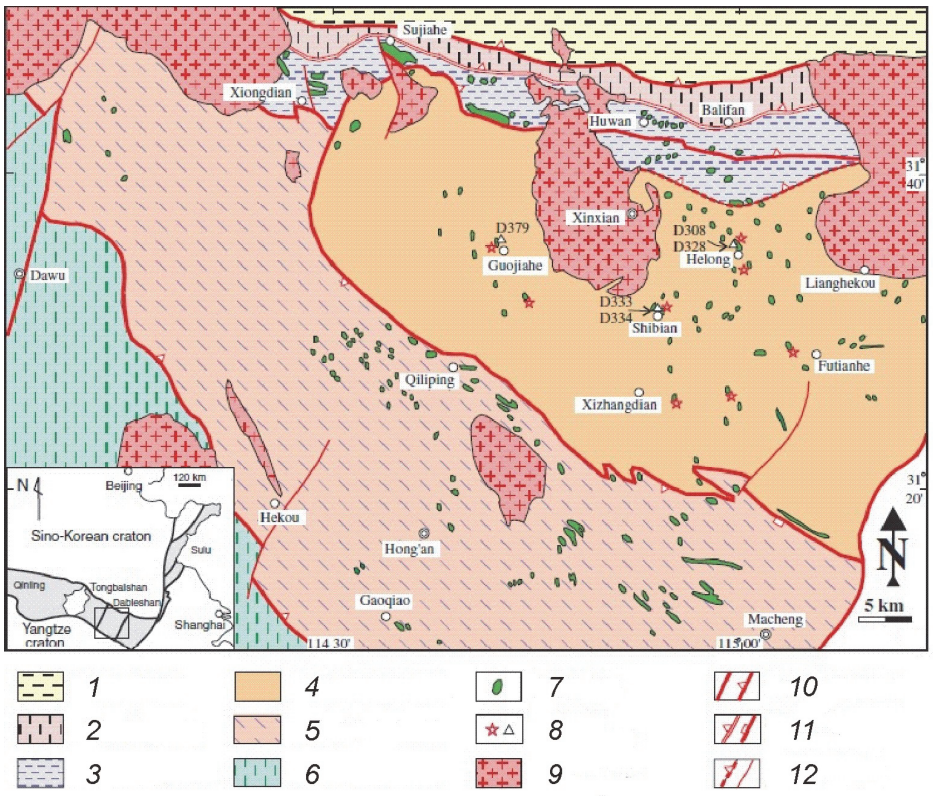

Fig. 1. Simplified geological map of the Dabie-Shan terrain showing the division of litho-structural units and distribution of eclogite blocks; inset to the map – location of the Dabie-Shan terrain in the Quinling–Dabie-Shan–Sulu orogen of China. Modified after [20]: *1–6* – units: *1* – Nawan flysch, *2* – Balifan melange, *3* – Huwan HP eclogite, *4* – Xinxian UHP eclogite, *5* – Hong'an HP eclogite, *6* – Mulanshan blue schist; *7* – eclogite block; *8* – coesite and sample localities; *9* – granites (*J–K*); *10* – major fault and thrust; *11* – suture and detachment faults; *12* – conjectured faults.

Among these suites, most pressure type facies of the regional metamorphism are suggested [18, 19] for the Upper Proterozoic rocks after appearance of glaucophane, phengite, albite, stilpnomelane, piemontite and spessartite [18, 19, 23]. The recognition of coesite- and diamond-bearing eclogites as well as systematic mineral paragenesises of eclogites, marbles and gneisses in the Dabie Mountains has significantly advanced studies of UHP supracrustal rocks and their geodynamic bearing on plate subduction to mantle depths of more than 100 km [3].

Sampling and analytical methods. We have studied metamorphic rocks in Yn-shan sector, eclogites and associated rocks in Shiankhuadnan area, apatite-bearing and intercalated rocks of the Dau phosphates district, and the Mulanshan blue schists with related rocks during field trips to the Dabie-Shan region. We observed shape and field relationships between marbles, eclogites, and blue schists with host and associated rocks. Special attention has been paid to the determination of glaucophane distribu-

tions within poor and rich in glaucophane sectors of the host rocks. Beside field investigation of glaucophane, we also collected a set of the carbonate samples from different localities named above.

We also carried out petrographic studying of thin sections to determine the crystallization order of minerals in gneisses, schists, marbles etc., which are typical for the Dabie-Shan region, as well as to check heterogeneity of individual minerals.

Taking into consideration the results of thin sections observations, microbeam analyses of glaucophane grains were carried out using SEM 106I scanning electron microscope equipped with an energy-dispersive detector on the previously cleaning and prepared samples by carbon fine film decoration. Set of the glaucophane grains with fresh surfaces without crushing of origin shapes has been used to determine character of its crystal surfaces, inner heterogeneity and coexisting phases. Analyses included general investigations of chemical composition of separate phases and estimation of components variations within grains. To calculate mass balance of the chemical elements we used the "Magallanes" program with data base for fundamental parameters of 92 elements.

The oxygen and carbon isotopic compositions in the whole-rock carbonates were analyzed in the Laboratory of Stable Isotopes (Institute of the Lithosphere of Marginal Seas, Moscow). Carbon dioxide was released from carbonates using $PbCl_2$. The relative difference in oxygen and carbon isotope ratios in CO_2 (gas) was measured on the mass spectrometer Varian MAT-250. The laboratory CO_2 was used as standard during isotopic measurement. The accuracy of $\delta^{13}C$ and $\delta^{18}O$ measurement in whole-rock samples was ± 0.1 and ± 0.2 ‰, respectively. The Craig correction was taken into consideration for the determination of $\delta^{13}C_{samp}$ (PDB) and $\delta^{18}O_{samp}$ (SMOW). The oxygen correction was taken into account for $\delta^{13}C_{samp}$ (PDB).

Character of glaucophane distribution in the host rocks. Field observations indicate irregular development of glaucophane in leucocratic mica-feldspar gneisses and its concentrations in melanocratic schists with thickness up to a few of decimetres (Fig. 2). Linear orientation of single needle shape glaucophane crystals along structural elements of the host rocks is similar and subparallel to elongation directions of glaucophane crystals within the schists as well as to geological boundaries of different lithological varieties of the rocks in general.

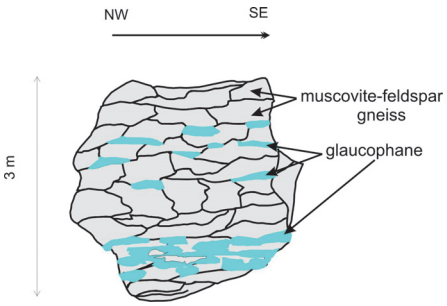

Fig. 2. Character of glaucophane single crystals distribution in leucocratic mica gneisses and enrichment of its crystals in glaucophane schists of the Mulanshan area.

There is no difference in size, colour, and shape of glaucophane crystals in places of its disseminations and concentration (Fig. 3). Inner structures of the crystals in both cases are similar and homogenous also (Fig. 4).

a *b*

Fig. 3. Glaucophane single crystals in leucocratic mica gneiss (*a*) and the concentrated crystals in glaucophane schist (*b*).

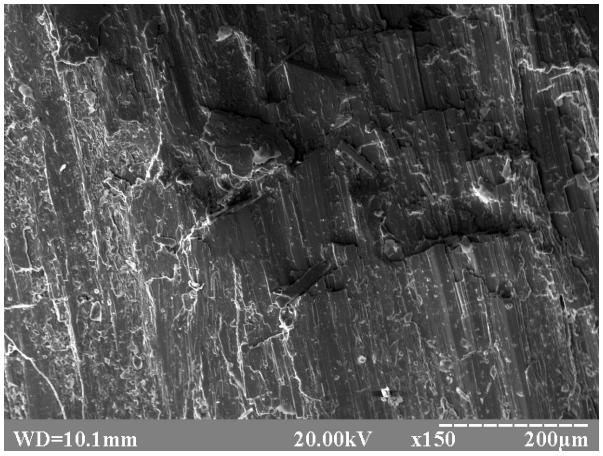

Fig. 4. Homogenous inner structures of the glaucophane crystals.

Chemical composition of glaucophane. Obtained data on chemical composition of the analyzed glaucophane have been calculated to get coefficients for K, Na and Ca to determine positions of the figurative points at the classification diagram for amphibole group according to recommendation of the IMA [17]. Actual K, Na and Ca values are located at the diagram very close to limits of the glaucophane field and some of them are out because of low Na concentrations.

To compare composition of glaucophane from the Dabie-Shan area and other regions of blue schists development [4, 5] we used a set of the compositional diagrams which take into account amount of SiO_2, Al_2O_3, MgO and Na_2O (Fig. 5).

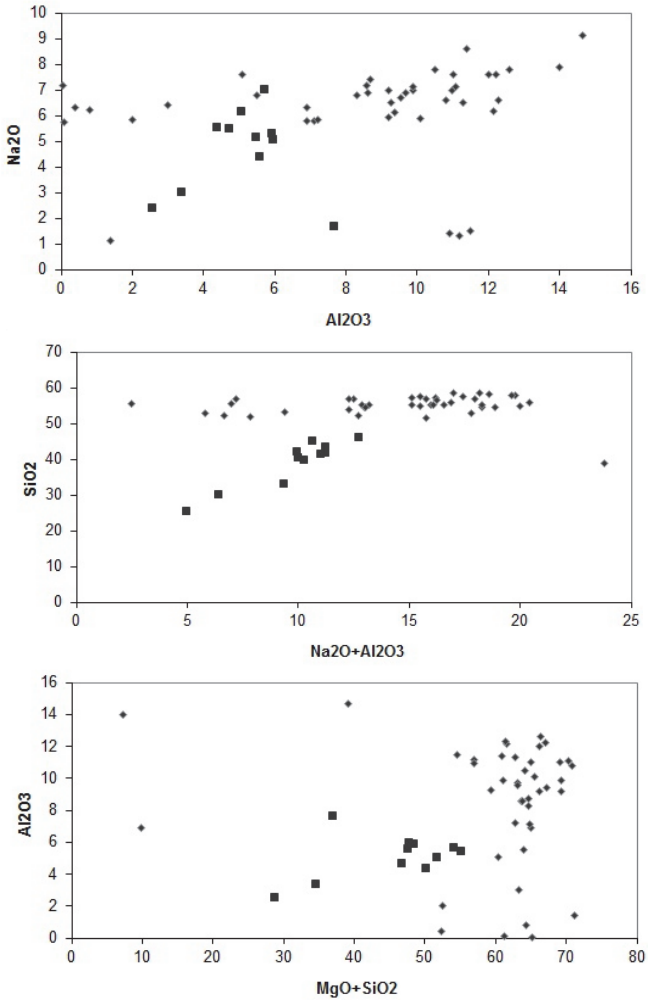

Fig. 5. Compositional diagrams for glaucophane after generalized data.
Icons in the form of squares – our data, rhombus – by [4].

Figurative points of both data groups on the diagrams commonly have similar location, but a part of glaucophane data from the Dabie-Shan terns from general tendency suggesting on its specific compositions. At the same time, compositional fields of glaucophane figurative points from etalon regions [4] are much more elongated than from the Dabie-Shan.

Isotope signatures in carbonates of the region. In addition to previously published results of isotopic investigations [3, 19], we studied isotopic composition of Carbon and Oxygen in carbonates of the marbles and apatite-bearing rocks from the Dabie-Shan region in hope to estimate the differences for these so heterogeneous in geological sense formations. Note, that Sheng Y.-F. et al. [3] suggested unusual high $\delta^{13}C$ values up to +5.7 ‰ (PDB) for carbonates associated with UHP eclogites in the

Dabie Mountains. The isotopic compositions of carbonates from apatite-carbonate rocks of all apatite deposits of the Precambrian Aldan Shield yield a scatter of $\delta^{13}C$ value from –0.5 up to +5.5 ‰ (PDB) and $\delta^{18}O$ value from +13.6 up to 22.2 ‰ (SMOW) [11]. Relatively high data for isotopically heavy carbon ($\delta^{13}C$ = +4.1 ‰, PDB) from the carbonates of the Dau apatite deposits are close to characteristics which we have found in carbonates formed in primary similar conditions [3]. So, isotopic evidences show preservation of the unusually high positive $\delta^{13}C$ values in the carbonates rocks. Similarly, there are not any indicators on significant oxygen isotopic difference in carbonate minerals since the time of their formation up to possible subduction of supracrustal rocks to mantle depths.

So, the character of glaucophane distribution within host rocks shows that the high pressure conditions could be not responsible for appearance of glaucophane among metamorphic rocks of the Dabie-Shane region. Concentration of the glaucophane in scales of a few of centimetres or even decimetres in separated lenses or layers we should observe unusually high gradients of pressure. Significant differences in chemical composition of poor and rich in glaucophane stratum support idea about important role in glaucophane crystallization suitable chemical composition of initial rocks. It is in accordance with origin of eclogites as primary sedimentary rocks [12, 21] in general, and in the Kokchetav region, particularly. We noted above about paradoxical distribution of diamond in the metamorphic rocks and presence here of eclogites as most poor in diamond rocks. Beside it, first publications on origin of Kazakhstan eclogites have been reported about their primary sedimentary nature [21]. So, even in this case the possible role of high pressures is minimal for appearance of diamond and similar indicator minerals.

Obtained isotopic data have been shown inert behaviour of CO_2 during minerals recrystallization and possibility to preserve of isotope marks on primary origin of carbonates in the Dabie-Shan region. Presence of quartz (or, as some authors indicated [18, 25], initial coesite) in association with dolomite in marbles and rich in carbonates rocks has been also indicated on low temperatures of their recrystallization and inert role of CO_2 in possible transformations. Abundance of different carbon-bearing mineral phases in assemblages with diamond, coesite, carbonates etc. is evidence for ideas about crystallization of minerals, which are determined as products of high pressure conditions, from other initial components and under less extreme limits of temperatures and pressures. Absent of diopside and relatively similar amounts of quartz and dolomite indicate much lower conditions of temperature than suggested (500–800 °C [14]) for retrograde recrystallization.

Sang Longkang (China University of Geosciences, Wuhan, China) is thanked for aid with the support for field trips to the Dabie-Shan region.

REFERENCES

1. Bushmin S. A. The scheme of mineral facies of metamorphic rocks / S. A. Bushmin, V. A. Glebovitsky // Zapiski RMO (Proceedings of the Russian Mineralogical Society). – 2008. – Pt. 137, N 2. – P. 1–15. (in Russian)
2. Bushmin S. A. Scheme of mineral facies of metamorphic rocks and its application to the Fennoscandian Shield with representative sites of orogenic gold mineraliza-

tion / S. A. Bushmin, V. A. Glebovitsky // Transactions of Karelian Research Centre of Russian Academy of Sciences. – 2015. – December. – P. 1–25. (in Russian)
3. Carbon isotopic anomaly in marbles associated with eclogites from the Dabie Mountains in China / Zheng Y. F., Fu B., Gong B., Wang Z. // J. of Geol. – 1998. – Vol. 106, N 1. – P. 97–104.
4. Dobretsov N. L. Glaucofane schist and eclogite-glaucofane schist complexes of USSR / N. L. Dobretsov // Proceedings of the IGG SO AN SSSR. – 1974. – Vol. 57. – 426 p. (in Russian)
5. Dobretsov N. L. Glaucophane schists and eclogites in the folded systems of northern Asia / M. L. Dobretsov, N. V. Sobolev // Ofioliti. – 1984. – Vol. 9. – P. 401–423. (in Russian)
6. Dobrzhinetskaya L. F. Frontiers of ultrahigh-pressure metamorphism: view from field and laboratory / L. F. Dobrzhinetskaya // Ultrahigh-Pressure Metamorphism: 25 Years after the Discovery of Coesite and Diamond / [Ed. by L. F. Dobrzhinetskaya, S. W. Faryad, S. Wallis et al.]. – London : Elsevier, 2011. – P. 1–39.
7. Dobrzhinetskaya L. F. Microdiamonds – Frontier of ultrahigh-pressure metamorphism. A review / L. F. Dobrzhinetskaya // Gondwana Research. – 2012. – Vol. 21. – P. 207–223.
8. Dobrzhinetskaya L. F. Nanometric inclusions of carbonates in Kokchetav diamonds from Kazakhstan: A new constraint for the depth of metamorphic diamond crystallization / L. F. Dobrzhinetskaya, R. Wirth, H. W. Green II // Earth and Planet. Sci. Letters. – 2006. – Vol. 243. – P. 85–93.
9. El-Shazly A. K. Interlayered eclogites, blueschists and epidote amphibolites from NE Oman: a record of protolith compositional control and limited fluid infiltration / A. K. El-Shazly, M. A Worthing, J. G. Liou // J. of Petrol. – 1997. – Vol. 38, N 11. – P. 1461–1487.
10. Eskola P. The mineral facies of rocks / P. Eskola // Norsk Geologisk Tidsskrift. – 1920. – Vol. 6. – P. 143–194.
11. Guliy V. N. Carbon and oxygen isotopic composition of carbonates from Precambrian apatite-bearing carbonate rocks of the Aldan shield / V. N. Guliy, H. Wada // Lithology and Minerals Resources. – 2004. – Vol. 39, N 3. – P. 243–253.
12. Letnikov F. A. Formation of diamonds within deap-seated tectonic zones / F. A. Letnikov // Doklady Academii Nauk SSSR (Proceeding of USSR Academy of Sciences). – 1983. – Vol. 371. – P. 433–435. (in Russian)
13. Leypunskiy O. I. On synthetic diamonds / O. I. Leypunskiy // Uspekhi Khimii (Progress Chemical). – 1939. – Vol. 8, N 10. – P. 1519–1534. (in Russian)
14. Low $\delta^{18}O$ eclogites from the Kokchetav massif, northern Kazakhstan // H. Masago, D. Rumble, W. G. Ernst [et al.] // J. Metamorphic Geol. – 2003. – N 21. – P. 579–587.
15. Microdiamond in high-grade metamorphic rocks of the Western Gneiss region, Norway / L. F. Dobrzhinetskaya, E. A. Eide, R. B. Larsen [et al.] // Geology. – 1995. – Vol. 23, N 7. – P. 597–600.
16. New genetic type of diamond deposits / L. D. Lavrova, V. A. Pechnikov, A. M. Pleshakov [et al.] // Science World. – Moscow, 1999. – 228 p. (in Russian)

17. Nomenclature of amphiboles: report of the Subcommittee on amphiboles and mineral names of the International Mineralogical Association (CNMMN IMA) / B. E. Leake, R. Woolley, W. D. Birch [et al.] // Zapiski RMO (Proceedings of the Russian Mineralogical Society). – 1997. – Pt. 137, N 6. – P. 82–102.
18. Okay A. I. Petrology of diamond and coesite-bearing metamorphic terrain Dabie Shan, China/ A. I. Okay // Eur. J. Mineral. – 1993. – Vol. 5. – P. 659–675.
19. Oxygen and hydrogen isotope geochemistry of gneisses associated with ultrahigh pressure eclogites at Shuanghe in the Dabie Mountains / Fu B., Zheng Y. F., Wang Z. [et al.] // Contrib. Mineral. Petrol. – 1999. – N 34. – P. 52–66.
20. Phase equilibria and metamorphic evolution of glaucophane-bearing UHP eclogites from the Western Dabieshan Terrane, Central China / Wei C. J., Li Y. J., Yu Y., Zhang J. S. // J. Metamorphic Geol. – 2010 – Vol. 28. – P. 647–666.
21. Rozen O. M. Diamond occurrence related to eclogite in Precambrian of Kokchetav massif / O. M. Rozen, Y. M. Zorin // Doklady Academii Nauk SSSR (Proceeding of USSR Academy of Sciences). – 1972. – Vol. 203. – P. 674–676. (in Russian)
22. Ruiz-Cruz M. D. Geochemical signatures and inclusions in apatite as markers of a hidden ultrahigh-pressure event (Betic Cordillera, Spain) / M. D. Ruiz-Cruz, C. Sanz de Galdeano, A. Santamara // J. of Geol. – 2016. – Vol. 124, N 3. – P. 277–292.
23. Sang L. The petrochemistry of the Lower Proterozoic rocks from the Dabieshan–Lyianynggang area, the South Eastern margin of the North China Platform / Sang L. // Precambrian Res. – 1991. – Vol. 39. – P. 65–76.
24. Shumilova T. G. Mineralogy of native carbon / T. G. Shumilova. – Ekaterinburg : UB RAS, 2003. – 315 p. (in Russian)
25. Zhang R. Y. Coesite inclusions in dolomite from eclogite in the southern Dabie Mountains,China: The significance of carbonate minerals in UHPM rocks / Zhang R. Y., Liou J. G. // Amer. Mineral. – 1996. – Vol. 81. – P. 181–186.

Стаття: надійшла до редакції 16.10.2016
прийнята до друку 02.11.2016

ОСОБЛИВОСТІ РОЗПОДІЛУ, СКЛАДУ ТА ПОХОДЖЕННЯ ГЛАУКОФАНУ З РАЙОНУ ДАБІ ШАН (КИТАЙ)

В. Гулій[1], І. Побережська[1], О. Ковтун[2]

[1]*Львівський національний університет імені Івана Франка,*
вул. Грушевського, 4, 79005 м. Львів, Україна
E-mail: vgul@ukr.net
[2]*Український державний геологорозвідувальний інститут,*
вул. Автозаводська, 78а, 04114 м. Київ, Україна
E-mail: ukrdgri@ukrdgri.gov.ua

Наведено дані про характер розподілу глаукофану в докембрійських породах району Дабі Шан (Китай) та особливості його складу. Глаукофан є головним мінералом порід верхньопротерозойського поясу Муланшан–Шангбакінг, складеного головно блакитними сланцями. У лейкократових породах поясу глаукофан розподілений нерівномірно, а в меланократових утвореннях він сконцентрований у глаукофанових сланцях, валовий хімічний склад яких відрізняється від лейкократових різновидів порід. З'ясовано, що неоднорідний розподіл глаукофану в різних породах, у тім числі тих, потужність яких становить перші дециметри, – це не наслідок впливу високого тиску (за якого звичайно утворюється глаукофан), це свідчення первинної природи вихідних утворень. Наявність нереально високих градієнтів тиску зумовила б появу й інших, подібних до глаукофану мінералів – коеситу, рутилу, лаусоніту тощо, а польові й петрографічні дослідження цього не підтвердили. Хімічний склад глаукофану з порід району Дабі Шан та поясів блакитних сланців різних регіонів світу подібний, хоча, звичайно, є певні локальні варіації.

Ізотопний склад C і O в карбонатах з різних типів порід досліджуваного регіону неоднорідний, однак загалом він свідчить про відсутність великомасштабних процесів перекристалізації за участю мобільного CO_2. Наявність у мармурах та збагачених карбонатами породах кварцу (або первинного коеситу, як уважають окремі дослідники) в асоціації з доломітом за відсутності діопсиду є тільки свідченням низьких значень температури можливих перетворень. "Закритість" карбонатних порід (як термодинамічної системи) підтверджено також ізотопними даними: і в мармурах, і в апатитоносних карбонатних породах, що з ними асоціюють, наявний головно ізотопно важкий вуглець з аномальними значеннями $\delta^{13}C$ – до + 5.7 ‰ (PDB) у мармурах і до + 4.1 ‰ (PDB) в апатитоносних карбонатних породах.

Наявність різних вуглецевмісних мінералів в асоціації з діамантом, коеситом, карбонатами тощо свідчить про специфічну вихідну форму їхніх компонентів – для появи їхніх твердих фаз високий тиск не потрібен.

Ключові слова: глаукофан, блакитні сланці, високий і надвисокий тиск, петрогенезис, ізотопи кисню й вуглецю, верхній протерозой, Дабі Шан, Китай.