BIULETYN PAŃSTWOWEGO INSTYTUTU GEOLOGICZNEGO 444: 187–190, 2011 R.

GEOCHEMICAL PECULIARITIES OF BASALTS OF THE TROSTYANETS VOLCANOGENIC COMPLEX (UKRAINIAN CARPATHIANS)

CECHY GEOCHEMICZNE BAZALTÓW KOMPLEKSU WULKANOGENICZNEGO TROSTYANETS (KARPATY UKRAIŃSKIE)

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Abstract. Studies of magmatic rocks of the Triassic–Lower Cretaceous ophiolite association are of great significance for geodynamic reconstructions of the evolution of the Ukrainian Carpathians. These are almond-stone basalts, clasto-lavas of basalts, and dykes of trachytes in the complex of volcanic rocks of the Trostyanets Stream. Rocks are allochthonous and hence studies of their petrochemical and geochemical properties are of great importance. Volcanites belong to the K-Na series of rocks poor in ferrimagnesian and rich in lithophylic elements; they developed on the ensialic substratum. Results of studies of two-phase fluid inclusions in calcite indicate that the gas phase constitutes 10 to 25 vol. % and is represented by CH_4 and its homologues – C_2H_6, C_3H_8 and C_4H_{10}. These data may indicate a possible formation of carbon and hydrocarbons by means of the Fischer-Tropsch reaction of hydrocarbon synthesis.

Key words: fluid inclusions, geochemical features, hydrocarbons, ophiolites, basalts.

Abstrakt. Badania skał magmowych asocjacji ofiolitowej triasu–kredy dolnej mają duże znaczenie dla geodynamicznej rekonstrukcji ewolucji ukraińskich Karpat. Dotyczy to bazaltów migdałowcowych, law z klastami i dajek trachitowych w kompleksie skał wulkanicznych potoku Trostyanets. Skały są allochtoniczne, toteż bardzo ważne jest badanie ich właściwości petrochemicznych i geochemicznych. Wulkanity należą do serii skał K-Na ubogich w pierwiastki żelazo-magnezowe i litofilne; tworzyły się w podwarstwie ensialicznej. Badania dwufazowych inkluzji w kalcycie pokazały, że faza gazowa zajmuje od 10 do 25% obj. i jest reprezentowana przez CH_4 i jego homologi – C_2H_6, C_3H_8 oraz C_4H_{10}. Dane te mogą wskazywać na możliwość tworzenia węgla i węglowodorów na drodze reakcji Fischer-Tropscha syntezy węglowodorów.

Słowa kluczowe: inkluzje fluidalne, cechy geochemiczne, węglowodory, ofiolity, bazalty.

Magmatic rocks of the Triassic–Lower Cretaceous ophiolitic association, the nature of which is interpreted ambiguously (Lyashkevich *et al*., 1995), are of great importance for geodynamic reconstructions of the initial stage of the evolution of the Carpathians. A great attention is given to investigation of petrochemical and geochemical characteristics of these rocks, as well as to the study of secondary processes, which have actively affected the rocks of the complex, taking the allochthonous occurrence of rocks into account.

Our investigations focused on a complex of volcanic rocks that form the cliffy outcrops, stretching for 2 km in a river-bed of the Trostyanets stream valley and its tributaries (Rakhiv district, Ukrainian Transcarpathia). It is represented by the flows of the Upper Jurassic–Lower Cretaceous basalts and clastolavas, cut by a number of parallel trachyte dikes. A predominant role in composition of the rocks belongs to basalts. Basalts are from grayish-brown to dark-violet in color, sometimes with a greenish and dark-gray hue.

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They are porphyric and have the almond-shaped fabric. Basalts underwent a significant influence of secondary processes such as carbonatization and development of chlorite aggregates. The flows of massive and almond-shaped basalts are alternated with clastolavas of basalts. The whole sequence is cut by a number of dikes of trachytes and diabases, which are strongly altered. The pillow singularity is frequently observed in basalts. The space between the pillows is filled in mainly with red or gray limestones. The almonds in basalts are filled in with calcite, zeolite and chlorite; their dimensions vary from several millimetres to a few centimetres. Chalcedony, quartz, analcime and prennite are rare. In some samples, there is organic matter in form of streaks and powder on basalts.

The reduced content of monocline pyroxene (diopside content 13.87%) and olivine (6.05%), as compared to plagioclase and potassium feldspar, which is reflected in the chemical composition of the rocks by the reduced content of Fe* = 8.3% (at Fe_2O_3/FeO ratio = 4.05) and MgO = 2.7%, is observed.

The content of alkali and phosphorus is high (6.65 and 0.47%, respectively). The SiO_2 content in basalts varies from 41.55 to 55.57% (averaging 45.53%). The K_2O/Na_2O ratio averages 0.46, which allows attributing the rocks to potassium-sodium series. The rocks show the high fractionation coefficient of about 75–78%, which points to a significant differentiation of the initial melt.

While analyzing the geochemical peculiarities of the basalts, an essential depletion of elements of the iron group should be pointed out, first of all of V and Cr, and an enrichment in lithophilous elements, especially in Rb, Ba, Sr. Rocks of the complex show a trend from low concentrations of Ni, Cr, Co, Sc, V to high ones of Zr, Nb, Ba, Rb, Th. This is visually reflected at the diagram of microcomponents Ni-Cr, where all the values for basalts occur in the ensialic area (Fig. 1). At the diagram of oceanic and continental basaltoids, all the values for basalts composition of the Trostyanets complex occur within the area of development of continental basalts (Fig. 2) (Borsuk *et al.*, 1987). These data allow treating the Trostyanets volcanogenic rocks as early volcanites, which developed on an ensialic substratum.

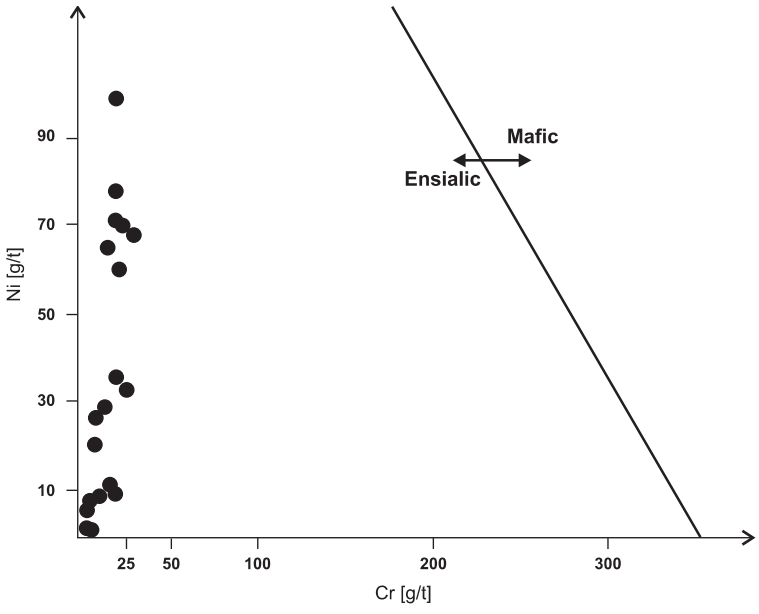

Fig. 1. Diagram of Ni-Cr for the average composition of basalt associations of fold areas and island arcs

Investigations of the fluid inclusions in the minerals of streaks and almonds in volcanic rocks of the Trostyanets volcanogenic complex showed the peculiarities of temperature regime and chemical composition of fluids along the process of post-magmatic mineral formation. Minerals of the complex are characterized by a variety of inclusions filled in with different fluids. There are two-phase gas-liquid inclusions (gas phase of about 10–20%), usually of uneven fill, and one-phase gas or liquid inclusions. Their dimensions vary within the 0.001–0.01 mm range and display irregular shapes. By phase composition, they are two-phase gas-liquid (gas phase of about 25%).

The results of fluid inclusions homogenization in calcite, which in streaks is paragenically related to laumontite, showed the following temperature intervals: for early-secondary fluid inclusions – within 300–330°C, for late secondary fluid inclusions – 210–260°C (Bondar *et al.*, 2010).

The data of mass-spectrometric chemical analysis of fluid inclusions in the minerals of streaks and almonds in volcanic rocks of the Trostyanets complex show the essential predominance of CH_4 (94.7–100.0 vol. %) in the content of volatile components (Table 1).

For calcite and zeolites, which form the fringe around the separate pillows, the existence of CH_4 and CO_2 in gas phase is established; for limestone, which fills the space between the pillows of basalt, CH_4 and its higher homologues (CO_2, N_2 and CO_2) were found. CO_2 was found only in zeolites from the calcite-zeolite streaks and in limestones (5.3 and 28.5 vol. %, respectively).

Nitrogen is present in limestones that are between the pillow space in basalts (12.3 vol. %), in zeolites from almonds in basalts (3.9 vol.%) and in quartz from the quartz-carbonate streak with organic matter (1.7 vol. %).

Apart from CH_4 (98.4 vol. %), the higher hydrocarbons were found in calcite: C_2H_6 – 0.9 vol. %, C_3H_8 – 0.6 vol. %, C_4H_{10} – 0.1 vol. %. They are also present in calcites (C_2H_6 – 0.6 vol. %, C_3H_8 – 0.3 vol. %) and zeolites (C_2H_6 – traces) from almonds.

Cases of predominance of methane with admixtures of other hydrocarbons in fluid inclusions in minerals are rather rare and are not typical of volcanic rocks. As it is based on the fact that most of fluid phases (up to 90%) which take part in endogenic geological processes are represented by the H–O–C system (H_2O, H_2, CO_2, CO and CO_4), the fluid inclusion data obtained for the Trostyanets volcanogenic complex may suggest a possible formation of carbon and hydrocarbons, in particular by the Fischer-Tropsch reaction of

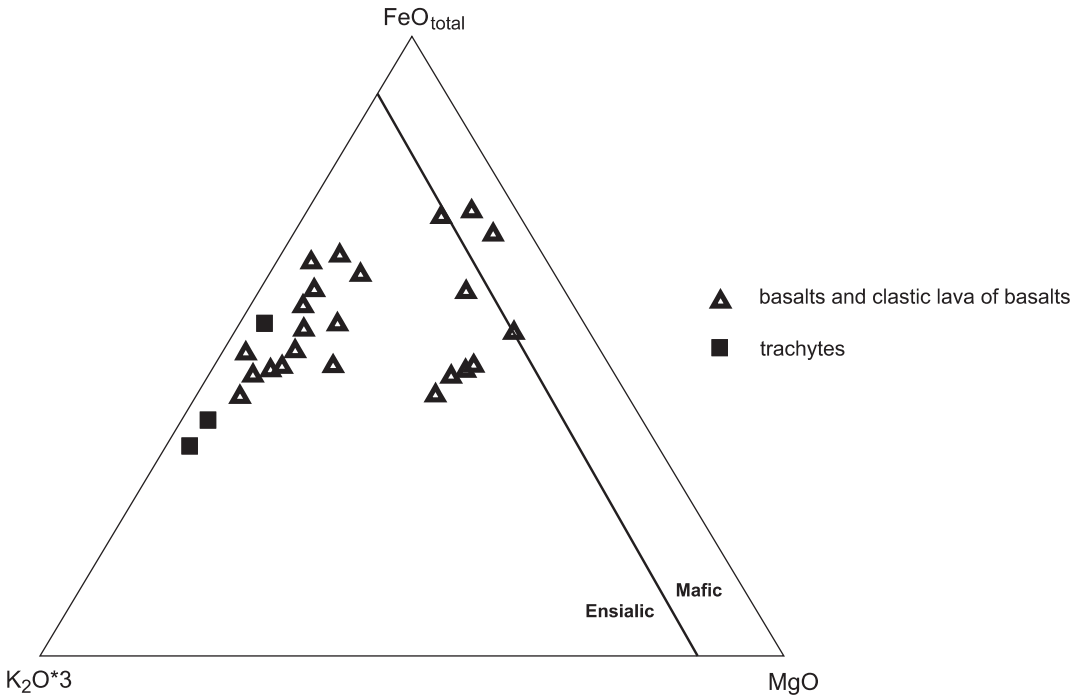

Fig. 2. Diagram of K_2O*3–FeO_{total}–MgO for the average composition of basalts of fold areas and island arcs

Table 1

Volatile composition of fluid inclusions in calcite, zeolites and quartz of veinlets, and almonds in volcanic rocks of the Trostyanets volcanogenic complex (data from the mass-spectrometry chemical analysis)

Sample number	Mineral	Components: [vol. %]					
		CO_2	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}
Tr6	calcite crystals	–	–	98.4	0.9	0.6	0.1
Tr1/1	calcite crystals from streaks	–	–	100.0	–	–	–
Tr1/1	zeolites from streaks	5.3	–	94.7	–	–	–
Tr2/1	calcite from almonds	–	–	99.1	0.6	0.3	–
Tr2/1	zeolites from almonds	–	3.9	96.1	trace	–	–
Tr5/1	quartz with organic matter from streaks	–	1.7	96.9	1.1	0.3	–
Tr5/1	calcite with organic matter from streaks	–	–	98.9	0.7	0.4	–
Tr5/1	organic matter	–	–	99.0	1.0	–	–

synthesis of hydrocarbons (Horita, Berndt, 1999; Foustoukos, Seyfried, 2004). The fluids were captured by micro- and macro-defects – forming fluid inclusions in the minerals and closed pores in volcanic rocks.

The compression forces of global nature prevailed during the Cretaceous in the field of tension of the study region with the ensialic substratum. The closure of the Tethys Ocean took place at that time. The tangential pressure appeared and constantly strengthened that have led to the formation of numerous fractures in rocks filled in calcite and zeolites with inclusions of CH_4 and higher hydrocarbons. There is no doubt that the Fischer-Tropsch synthesis of CH_4, C_2H_6 and C_3H_8 takes place in aqueous solution at elevated temperatures and in the presence of metallic (Fe–Ni–Cr) catalysts, which are common in basalts and trachytes of the Trostyanets volcanogenous complex.

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