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The simultaneous occurrence of hydrocarbons and metallic sulphides. An example of devonian dolomites at Józefka, Holy Cross Mountains, Poland

Introduction

The occurrence of hydrocarbons and ore mineralization, permitting the identification of their inter-relationships, in the quarry of Devonian limestone and dolomite located on the slopes of the Józefka hill, south of Górno village, has been recorded. The occurrence of bituminous substances accompanied by ore and non-ore mineralization has been noticed for a long time in many areas of the Holy Cross Mountains (Czermiński 1960; Łyczewska 1967; Nieć 1968; Czechowski et al. 1994; Salwa 1995). They were recorded, usually accompanied by calcite veins, dolomite veins and crystalline dolomite nests, mostly in the Łagów area (Łyczewska 1967). The quartz veins with accompanying bitumens has also been recorded (Czermiński 1960; Salwa 1995). It was assumed that their trace amounts in the asphaltite-like forms observed in the iron sulphide deposit in Rudki are a product of the movement of bitumens originally contained in the rock (Nieć 1968). The occurrence of ozokerite, graphitic substance, calcite, quartz, and ore minerals (chalcopyrite) in cracks has been found in the western part of the Holy Cross Mountains, in the Frasnian bituminous limestones

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(Czechowski et al. 1994). The abundance of hydrocarbon, ore, and non-ore mineralization in Józefka suggests their common origin.

1. Geological background

The limestone and dolomite quarry in Józefka is located in the western part of the Holy Cross Mountains, in the Kielce Synclinorium, on the southern wing of the Górna anticline. Thin-bedded dark gray, Frasnian micritic limestones and white-creamy "sugar-like" dolomites overlain by greenish dolomite-illite rocks as well as red hematite-bearing are exposed in the quarry (Phot. 1). These dolomites are a product of hydrothermal transformation (Migaszewski 1990; Nieć and Pawlikowski 2015). The contact zone between the dolomites and the tectonically disturbed Upper Devonian limestones is located along the NW-SE fault. Dolomites and limestones are heavily karsted. Parts of the collapsed Triassic sandstone cover are well-preserved in karst sinkholes (Phot. 2).

Phot. 1. Józefka quarry. NW wall of the excavation.
The contact zone between the Upper Devonian limestones (W), sugar-like dolomites (D), dolomite-illite rocks and hematite-bearing rocks (H); b – bitumen occurrence (see Phot. 3)

Fot. 1. Ściana NW kamieniołomu w Józefce.
Kontakt wapieni gónodewońskich (W), dolomitów „cukrowatych" (D) i skał dolomitowo-illitowych i hematytonośnych (H); b – wystąpienie bituminów (zob. fot. 3)

The region of the Józefka mine has long been known for ore and non-ore mineralization (Czarnocki 1936; Rubinowski 1966). Lead ores were mined in this region in the first half of the 19th century. In addition, calcite veins with chalcopyrite, galena, pyrite, and barite inclusions were also observed in Frasnian limestones. In the 1930s and in 1955, the occurrence of barite was examined with the use of excavations located to the north of the present quarry (Czarnocki 1936; Rubinowski 1966).

Phot. 2. Triassic sandstones in a karst sinkhole

Fot. 2. Piaskowce triasowe w kotle krasowym

2. Material and methods of research

Based on the observations carried out in the exposures of the Józefka quarry, the samples of rocks containing ore mineralization and hydrocarbons were collected for detailed analysis. The standard transmitted light microscopic (petrographic) analysis of rocks has been performed. The identification of ore minerals and observations of their occurrence forms were carried out using a binocular magnifying glass and preparations polished under reflected light. Selected samples were subjected to the X-ray phase analysis using a Rigaku diffractometer and Cu Kα radiation. The interpretation of the results was carried out using the XRAYAN program. To confirm the results of the determination of minerals, a microanalysis of the chemical composition was carried out using a FEI QUANTA 200 FEG scanning electron microscope.

The chemical analysis was performed in AcmeLabs (Canada). A sample with a weight of approximately 1kg was collected and ground to a size of 2 mm. After homogenization and reduction, a 250 g sample was ground to 75 m grain size. For the needs of the analysis, the samples were decomposed by fusing with lithium borates with the use of "aqua regia".

3. The mode of occurrence of hydrocarbons and ore mineralization

The abundant occurrence of hydrocarbons can be observed in the zones of intense tectonic deformation. These include concentrations of liquid oil in cracks and intense saturation of surrounding rocks with hydrocarbons in the vicinity of cracks and stratification planes (Phot. 3A, 3B, 4, and 5).

Phot. 3. The occurrence of hydrocarbons in fracture zones. General (A, wall heights 10 m) and detailed (B) view

Fot. 3. Wystąpienie węglowodorów w strefach spękań.
Widok ogólny (A, wysokość ściany 10 m) i szczegółowy (B)

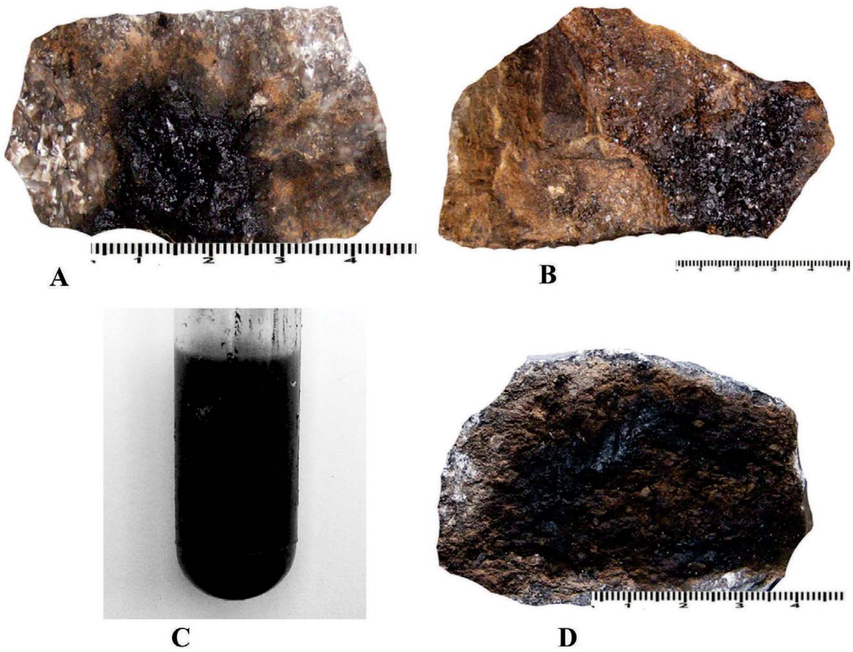
Phot. 4. Impregnation of limestones by hydrocarbons along stratification planes

Fot. 4. Wystąpienie węglowodorów w strefach spękań

In addition to hydrocarbons, sulphides, accompanied with calcite and forming veins cutting limestone, can also be observed in cracks. The mentioned hydrocarbons occur along the border of the host rock or between individual generations of the filling calcite (Phot. 6).

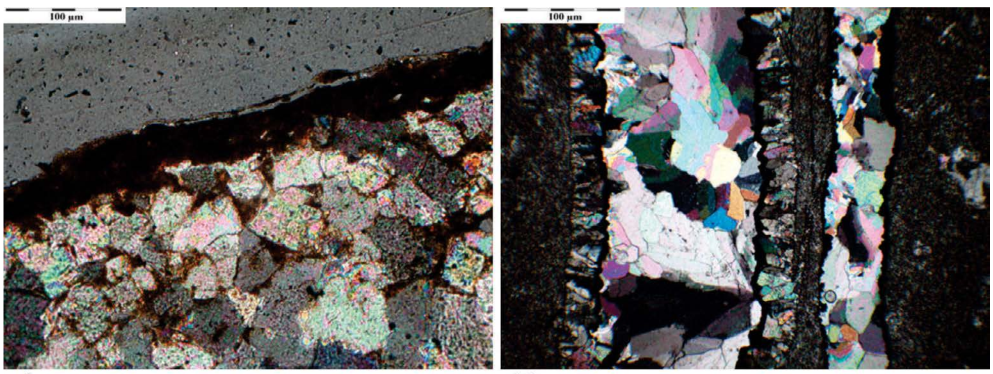
Pyrite, accompanied by chalcopyrite, is the dominant sulphide. In addition to the hydrocarbon occurrence zone, chalcocite and galena accompanied by calcite and, less commonly, barite can also be found (Phot. 7). The limestones in the vicinity of some of the veins are sometimes discoloured.

Sulphides are often weathered. Their oxidation products included: hematite, chrysocolla (Phot. 7F), malachite, azurite, goethite, manganite, and pyrolusite.



Phot. 5. A, B – black concentrations of liquid hydrocarbons in dolomite,
C – hydrocarbons isolated from Devonian limestones extracted with gasoline (analytical reagent grade),
D – concentrations of solid hydrocarbons

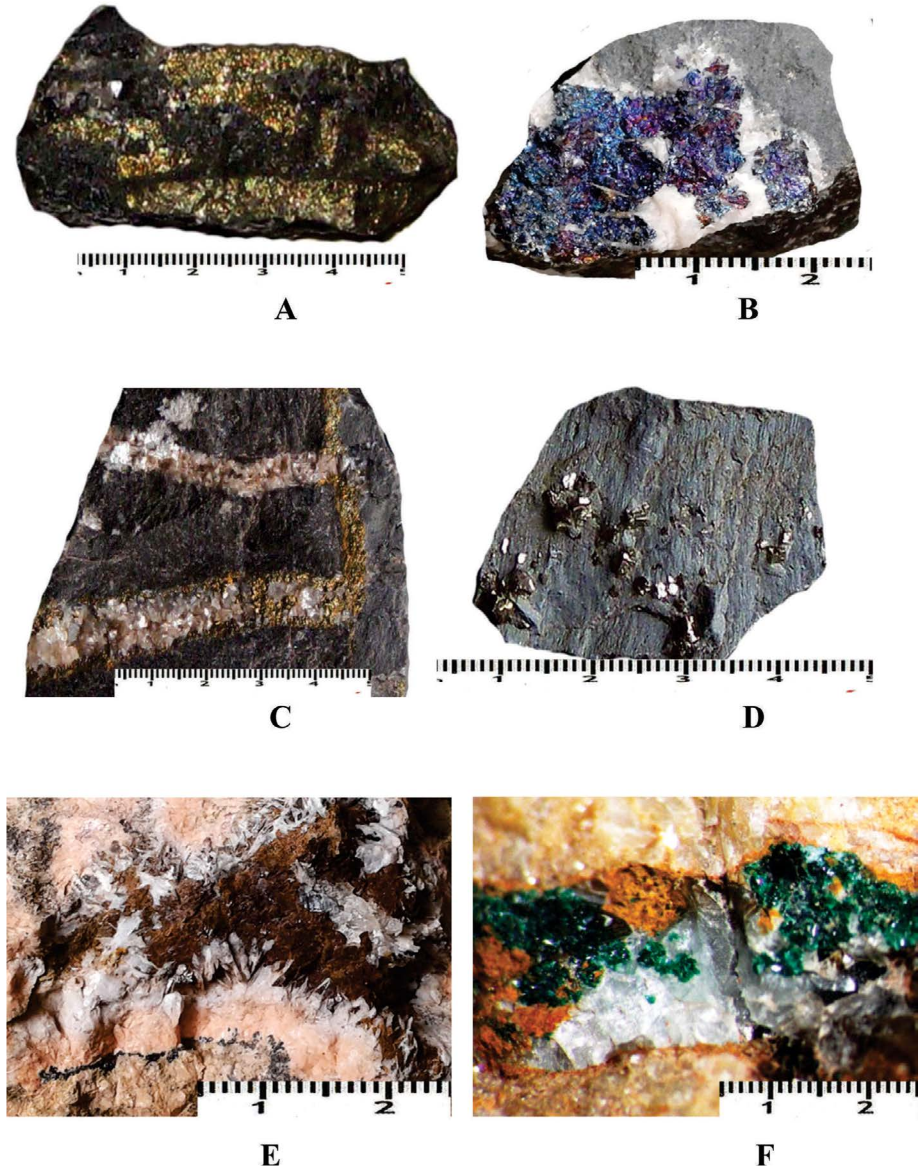
Fot. 5. A, B – skupienia węglowodorów ciekłych, C – Węglowodory wydzielone z wapieni dewońskich,
wyekstrahowane benzyną (cz.d.a.), D – skupienia węglowodorów stałych



A B

Phot. 6. A – asphaltite-like coatings on the surface of the slickenside,
B – calcite veins with a complex structure; there is a clearly visible accumulation of hydrocarbons at the contact zone between veins and limestone and at the border of the calcite generations

Fot. 6. A – asfaltytopodobne powleczenia na powierzchni lustra tektonicznego,
B – żyłki kalcytowe o złożonej budowie; na kontakcie żyłek z wapieniem
oraz na granicy generacji kalcytu widoczne nagromadzenie węglowodorów



Phot. 7. A – pyrite and marcasite with chalcopyrite in dolomite with a high content of dispersed hydrocarbons, B – chalcocite co-occurring with calcite, C – ore-quartz veins in bituminous limestone, D – idiomorphic pyrite crystals in the tectonic zone crystallized on the slickenside, E – pink, crystalline barite co-occurring with hematite and black manganese oxides, F – chrysocolla co-occurring in dolomite with calcite and hydrated iron oxides

Fot. 7. A – piryt i markasyt z chalkopirytem w dolomicie z dużą zawartością rozproszonych węglowodorów, B – chalkozyn współwystępujący z kalcytem, C – żyłki kruszcowo-kwarcowe w wapieniu bitumicznym, D – idiomorficzne kryształy pirytu w strefie tektonicznej wykrystalizowane na lustrze tektonicznym, E – różowy, krystaliczny baryt współwystępujący z hematytem i czarnymi tlenkami manganu, F – chryzokola występująca w dolomicie wraz z kalcytem i uwodnionymi tlenkami żelaza

Limestone cracks are often covered with a black substance (Phot. 8). Infrared tests (Fig. 1) have confirmed that it shows features similar to graphite. In addition, concentrations of sulphides, including pyrite, sphalerite, and galena are also reported. Their presence is confirmed by the X-ray phase analysis of a black substance from the slickenside. Furthermore, the analysis has shown the presence of barite, quartz, illite, and lizardite. The graphitization of organic substances observed in fault zones is the result of the friction of rock blocks during their movements along the zones of tectonic disturbances and the associated thermal effects. It is suggested that this is related to violent seismic events (Kuo et al. 2017).

Phot. 8. Hydrocarbon coatings with sulphides on the slickenside

Fot. 8. Powleczenia węglowodorowe z siarczkami na lustrze tektonicznym

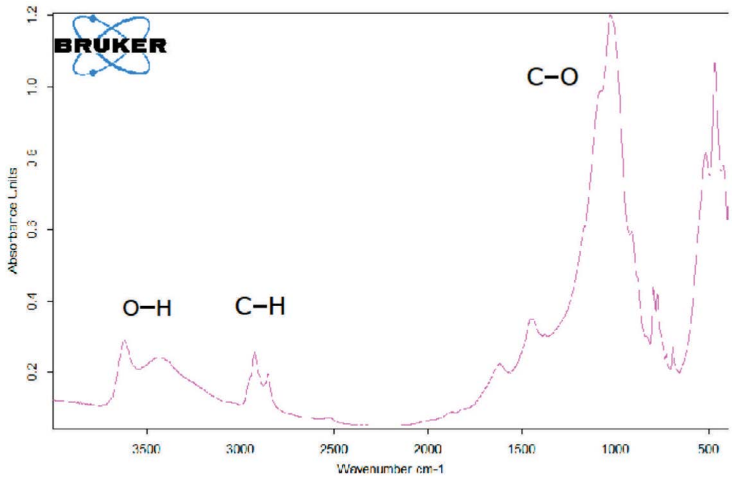


Fig. 1. The infrared absorption spectroscopy of hydrocarbons from the veins within the dark limestones

Rys. 1. Widmo spektroskopii absorpcyjnej w podczerwieni węglowodorów z żyłki tnącej ciemne wapienie

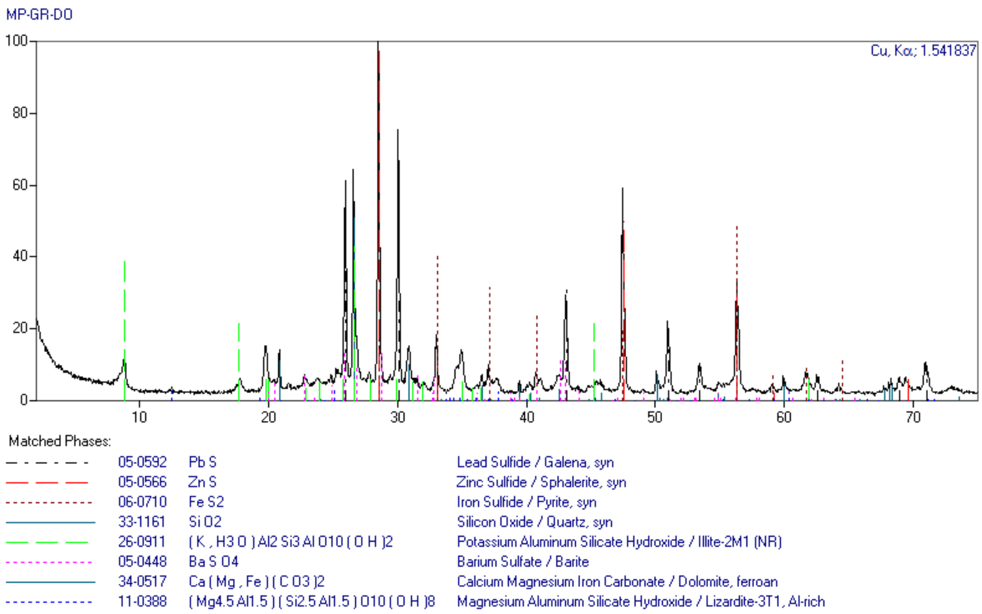


Fig. 2. The X-ray diffraction pattern of the material of the black coating on slickenside developed in the area of hydrocarbon occurrence

Rys. 2. Dyfraktogram rentgenowski materiału z czarnego lustra tektonicznego rozwiniętego w strefie występowania węglowodorów

4. Rocks hosting mineralization and hydrocarbons

The occurrence of hydrocarbons is recorded in the Upper Devonian limestones. The chemical analysis has shown that the limestones hosting hydrocarbons and mineralization are not distinguished by special features; however, a high content of Sr and vanadium, which indicates specific conditions of their sedimentation, should be taken into account.

5. The relationship between bitumen and ore mineralization

The occurrence of ore deposits in the vicinity of hydrocarbon deposits is recorded in many areas; furthermore, the co-occurrence of sulphide mineralization and hydrocarbons is found in many ore deposits. This is explained in different ways (Manning 1986; Parnell 1991, 1993; Saitilan et al. 2016):

- As a result of the reduction of sulphates by hydrocarbons (with or without the participation of bacteria) and the precipitation of sulphides by the resulting hydrogen sulphide,

Table 1. The results of chemical analysis of limestones from the Józefka mine

Tabela 1. Wyniki analiz chemicznych wapieni z kopalni Józefka

%		Ppm			
SiO_2	14.42	Ba	94	La	16.1
Al_2O_3	3.95	Sr	323.1	Ce	33.4
Fe_2O_3	1.35	Rb	40.2	Pr	3.78
MgO	4.63	Cs	2.5	Nd	16.3
CaO	37.71	Ga	4.1	Sm	3.18
Na_2O	0.04	Nb	4.1	Eu	0.74
K_2O	1.39	Th	3.1	Gd	3.26
TiO_2	0.2	U	2	Tb	0.46
P_2O_5	0.04	V	114	Dy	2.61
MnO	0.05	Mo	1.6	Ho	0.54
S	0.58	Cu	8.9	Er	1.46
		Pb	23.3	Tm	0.19
		Zn	13	Yb	1.21
		Ni	10.7	Lu	0.19
		Co	9	Y	17.2
		As	12.4	Sc	4
		Zr	45.7		
		Hf	1.1		

- Common migration routes for metal-bearing solutions and hydrocarbons, often coming from the same source – bedrocks, usually black slates,
- Transport of metals in solutions containing organic compounds, presumably, organometallic.

The occurrence of sulphide mineralization in crude oil reservoir rocks recorded in oil deposits in the North Sea suggests a common migration of hydrocarbons and metal-bearing solutions (Baines et al. 1991).

The coexistence of sulphide and hydrocarbon mineralization recorded in the Holy Cross Mountains suggests their common origin. The observed sulphide complex, including chalcopyrite, pyrite, marcasite, covellite, chalcocite, and galena, can be considered as a product of low-temperature hydrothermal activity, also recorded in other regions of the Holy Cross Mountains (Rubinowski 1971). The analysis of liquid inclusions in carbonates (Migaszewski

1990) and the mineral paragenesis of such mineralization observed in other regions (Nieć 1968; Nieć and Pawlikowski 2015) suggest a temperature range of approx. 100 to 150°C. This is the temperature range of the oil window, which suggests the common origin of sulphides and hydrocarbons and may explain their co-occurrence and, possibly, the same source.

It is suggested that the Silurian and Ordovician shales occurring at greater depths are the primary source of hydrocarbons (Łyczewska 1967). The source of sulphides could be either the same shales or transitional beds from the Lower to Middle Devonian, enriched in sulphides (Kowalczewski and Wróblewski 1974; Wróblewski 1989). Their association with intrusions of igneous rocks – diabases and lamprophyres present in the Holy Cross Mountains may also be supposed (Rubinowski 1969).

The strict coexistence of sulphide and hydrocarbon mineralization suggests organometallic compounds as metal carriers (Manning 1986). The presence of elevated contents of metallic elements is found in natural gas (Kucha et al. 1993; Lubaś 1993) and crude oil (Wilhelm and Bloom 2000). Their mode of occurrence has not been studied. It is suggested that these may include methyl metallic compounds. As a result of their reaction with H_2S formed by sulphate reduction, the sulphides are precipitated:

$$CH_4 + SO_4^{2-} = H_2S + CO_2 + 2H_2O$$

$$CH_2Me + H_2S = MeS + CH_4$$

Both sulphide and hydrocarbon mineralization in the Józefka mine have no practical significance. However, they may indicate areas of heavier sulphide mineralization and, possibly, economic importance in the neighboring or deeper parts (in the dolomite substrate).

The formation of metalliferous hydrocarbons may be associated with the transformation of organic compounds into hydrocarbons. This process involves the concentration of carbon and hydrogen while other elements are released from transforming organic compounds. For example, the transformation of natural sugars, such as glucose or fructose (Fig. 3) may produce methane, but also – CO_2.

However, if not all carbon valences are saturated by the hydrogen in the newly formed hydrocarbon, and free cations are found at the generation site, they can be attached to free

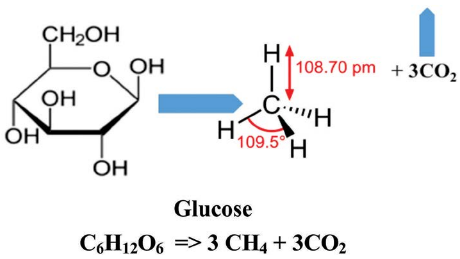
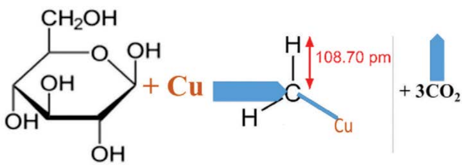


Fig. 3. An example of a theoretical structural transformation of a simple sugar – glucose into methane

Rys. 3. Przykład teoretycznej strukturalnej transformacji prostego cukru – glukozy w metan



CH_2Cu, in a further reaction with e.g. H_2S => $CH_4 + CuS$ (covellite)

Fig. 4. The theoretical reaction of covellite formation from a sugar (glucose) complex subjected to hydrocarbon-metal transformation into CH_2Cu

Rys. 4. Teoretyczne reakcja powstawania kowelinu z kompleksu cukru (glukozy) ulegającego przebudowie węglowodorowo-metalowej w CH_2Cu

chemical bonds (Fig. 4). This phenomenon may involve the generation of more complex hydrocarbons and hydrocarbon-metal complexes.

Conclusions

The observed coexistence of hydrocarbons and ore mineralization supports the hypothesis of their common origin and the possible same source of both that can be black shales with elevated metals content, which have been long considered as a source for metalliferous solutions (Marmo 1960). It is possible that hydrocarbons in organometallic compounds are metal carriers, which would explain their coexistence. To clarify these issues, there is a need for broader, regional geochemical and metallogenic studies, the results of which may be essential in determining whether the ore mineralization indicates the potential for hidden mineral deposits.

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THE SIMULTANEOUS OCCURRENCE OF HYDROCARBONS AND METALLIC SULPHIDES. AN EXAMPLE OF DEVONIAN DOLOMITES AT JÓZEFKA, HOLY CROSS MOUNTAINS, POLAND

Keywords

Poland, Hydrocarbons, ores, Devonian

Abstract

Ore and non-ore mineralization in cracks filled with hydrocarbons in the dark grey Upper-Devonian limestone has been found in the Józefka quarry of Upper Devonian limestone and dolomite near the Górno village near Kielce at Holy Cross Mts. Poland. Hydrocarbons in the liquid form and iron and copper sulphides appears hear in the fault zone as joints filling. The wall rocks are impregnated by hydrocarbons giving them black color. Hydrocarbon impregnations appears also following the bedding planes The coexistence of ore mineralization and hydrocarbon suggests their common origin and migration from deep-seated sources, that may be the Silurian Ordovician or Lower to Middle Devonian black shales. The metallic-hydrocarbon compounds were suggested as metals carrier.

Ore and non-ore mineralization in cracks filled with hydrocarbons in the dark grey Upper-Devonian limestone has been found in the Józefka quarry of Upper Devonian limestone and dolomite near the Górno village near Kielce at Holy Cross Mts. Poland. Hydrocarbons in the liquid form and iron and copper sulphides appears hear in the fault zone as joints filling. The wall rocks are spotty impregnated by hydrocarbons giving them black color. Hydrocarbon impregnations appears also following the bedding planes The coexistence of ore mineralization and hydrocarbon suggests their common origin and migration from deep-seated sources, that may be the Silurian Ordovician or Lower to Middle Devonian black shales. The metallic-hydrocarbon compounds were suggested as metals carrier.

WSPÓŁWYSTĘPOWANIE WĘGLOWODORÓW I SIARCZKÓW METALI. PRZYKŁAD DOLOMITÓW DEWOŃSKICH W JÓZEFCE W GÓRACH ŚWIĘTOKRZYSKICH

Słowa kluczowe

Polska, rudy, weglowodory, dewon

Streszczenie

W kamieniołomie wapieni górnodewońskich w Józefce k. miejscowości Górno k. Kielc w Górach W kamieniołomie wapieni górno dewońskich w Józefce koło miejscowości Górno koło Kielc w Górach Świętokrzyskich stwierdzono współwystępowanie węglowodorów i siarczków żelaza i miedzi w spękaniach w strefie uskokowej. Węglowodory występują także w formie rozproszonej, plamiście w otaczających wapieniach nadając im czarną barwę oraz wzdłuż płaszczyzn ich warstwowania. Współwystępowanie węglowodorów i siarczków metali sugeruje ich wspólną genezę i migrację z głęboko położonego źródła. Skałami macierzystymi, mogły być czarne łupki występujące w utworach

syluru i ordowiku oraz na pograniczu dewonu dolnego i środkowego wyróżniane jako wzbogacony w metale „poziom rudonośny". Zwrócono uwagę, że nośnikiem metali mogły być związki metaloorganiczne.

W kamieniołomie wapieni górno dewońskich w Józefce koło miejscowości Górno k. Kielc w Górach W kamieniołomie wapieni górno dewońskich w Józefce koło miejscowości Górno k. Kielc w Górach Świętokrzyskich stwierdzono współwystępowanie węglowodorów i siarczków żelaza i miedzi w spękaniach w strefie uskokowej. Węglowodory występują także w formie rozproszonej, plamiście w otaczających wapieniach, nadając im czarną barwę oraz wzdłuż płaszczyzn ich warstwowania. Współwystępowanie węglowodorów i siarczków metali sugeruje ich wspólną genezę i migrację z głęboko położonego źródła. Skałami macierzystymi mogły być czarne łupki występujące w utworach syluru i ordowiku oraz na pograniczu dewonu dolnego i środkowego wyróżniane jako wzbogacony w metale „poziom rudonośny". Zwrócono uwagę, że nośnikiem metali mogły być związki metaloorganiczne.