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OIL CHARGING AND GAS FORMATION EPISODES IN THE DEVONIAN CARBONATES OF THE LUBLIN BASIN (SE POLAND)

Abstract: Laser *in-situ* stable carbon and sulphur isotope analysis from carbonate diagenetic minerals formed during hydrocarbon charging allowed to distinguish the chemical processes which took place in the Devonian carbonate reservoir during gas field formation. Two different in time episodes of oil migration from sub-basins with source rocks and subsequent two events of oil cracking into gas were accompanied by bacteria-influenced processes in pore spaces.

Keywords: oil migration, gas formation, bacterial influence, carbonate reservoir, Devonian, Lublin

INTRODUCTION

Gas accumulation of the Ciecierzyn-Mełgiew Field in the Devonian carbonate reservoir of the central part of Lublin basin, SE Poland (Fig.1), is the object of this study. Petrographic and isotope studies of inorganic products of diagenesis allowed to determine two independent in time and space directions of oil migration into the field area, and succession of oil maturation and cracking into gas processes with thermochemical sulfate reduction events. Active basin processes during extension and next strike-slip movements of Variscan time created fast subsiding basins with source rock complexes which episodically expulsed hydrocarbons into active compartment systems of carrier beds and reservoir rocks. During these processes conditions of formation of the water-hydrocarbon system influenced by bacteria significantly varied, as recorded by the isotope system.

ANALYTICAL TECHNIQUES

Rock samples were firstly examined by means of the standard petrography (transmitted light microscopy and SEM), cathodoluminescence (CL), and fluorescence (UV) at the Laboratories of the Geological Bureau – GEONAFTA Regional Division Wołomin in the Polish Oil and Gas Company (recently Petrogeo Ltd.), and the Institute of the Earth Sciences of the Polish Academy of Sciences in Cracow and Warsaw, Poland.

The main part of the isotope analyses of ^{13}C in calcite and saddle dolomite cements was made by the *in situ* laser extraction method (Smalley *et al*. 1989) at the laboratory of Scottish Universities Environmental Research Centre (SUERC) in East Kilbride, Scotland. The sample of CO_2 for the analyses was released according to the reaction:

1) $2CaCO_3$ (sample) => $CO_2 + CO + ½O_2 + 2CaO$.

The isotope ratios were measured on the Finnigan Mat mass spectrometer model 251, with a mean reproducibility ±0.36 ‰. The laser made analytical pit of diameter 100 µm, with $3\times10^4 \mu m^2$ surrounding influence area (SUERC method). Earlier samples were cleaned by Soxhlet extraction with xylene and methylated spirits (Trewin 1988) to remove bitumens. All ^{13}C data are reported as δ in per mil (‰) relative to the Pee Dee belemnite (PDB).

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Sulfur isotope analyses from anhydrite, pyrite and elemental sulfur were made following the method of Holt and Engelkemier (1970), and Robinson and Kusakabe (1975) on the MI-1201W mass spectrometer at the Radiocarbon Laboratory of Institute of Geochemistry, and Physics of Minerals (DRGE IGMOF) of the Ukrainian Academy of Sciences in Kiev, Ukraine. The isotopic values of ^{34}S are shown as δ in per mil (‰) relative to the Canyon Diablo troilite (CDT) standard with reproducibility of ±0.3 ‰.

GEOLOGIC SETTING

The Ciecierzyn-Mełgiew gas field is located in the south-eastern part of the Mazowsze-Lublin trough of the central part of Lublin basin, SE Poland, which is involved in the system of NW-SE dislocations and faults with slightly folded sequences (Fig. 1).

Gas accumulation of the Ciecierzyn-Mełgiew field was found in the Middle and Late Devonian (Givetian and Frasnian) dolostones and limestones of peritidal-sabkha carbonate platform, and coral-stromatoporoid-renalcid patch reefs deposits of the Modryń formation (Fig.1).

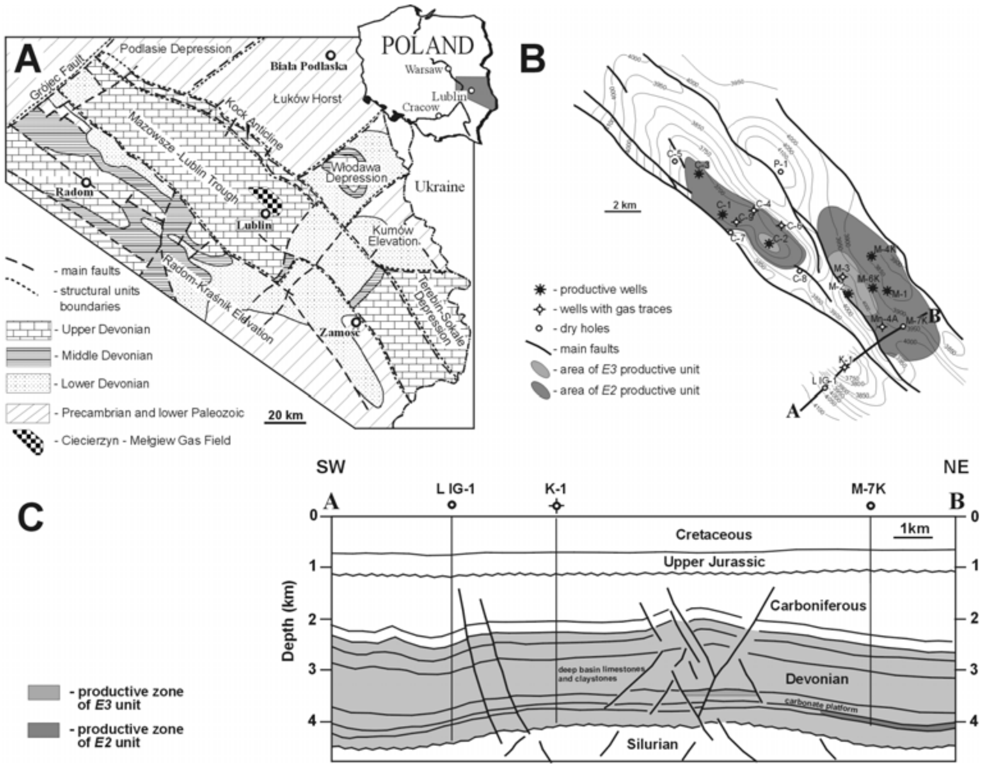

Fig. 1. (A) Structural map of the Lublin basin area. (B) Ciecierzyn – Mełgiew gas field. (C) Cross section A-B (location given on the picture B) through gas field area. See strike-slip structure in the center, typical for Variscan tectonic. On the pictures A & B gas productive zones are shown.

Productive units of Modryń formation (Fig. 1) are sealed by internal impermeable layers inside the peritidal-sabkha cycles (*E2* productive unit) and deep-marine claystones intercalated with limestones (*E3* productive unit of carbonate platform deposits) of the Fammenian Bychawa formation (Fig. 1C).

SOURCE ROCKS AND GAS CHARACTERISTIC

Recently, in all productive wells and wells with gas traces there are petroleum decomposition products in forms of high concentration methane gas and solid bitumens (pyrobitumens); they are still recently migrating oil residues in the *E2* and *E3* productive units, with insignificant light oil appearance in the *E3* unit.

Despite of earlier proposed sources of hydrocarbons in Silurian and Ordovician deposits (Calikowski *et al*. 1971; Mitura 1971; Simon Petroleum Technology 1993), their origin from Famennian limestones and claystones of Bychawa formation (Fig. 1) in the central Lublin basin area (Calikowski, Gondek 1967; Kotarba *et al*. 1998) seems to be the most reasonable. The correlation on the basis of stable carbon isotopes of oil traces in the gas reservoir and bitumens in the Bychawa formation confirms the Devonian source rock as correctly recognised (*see* Kotarba *et al*. 1998). Chromatographic analysis of organic matter compounds marks kerogen type II as having marine algae source as typical of hydrocarbons of the average hydrocarbon potential of the Bychawa formation. The isotopic record of field gas (*cf.* Kotarba 1997, as given in Table 1) clearly indicates its thermogenic nature.

Table 1. Isotope gas composition (Kotarba 1997).

Gas well	Depth (m)	Productive unit	$\delta^{13}C$ (CH_4)	$\delta^{13}C$ (C_2H_6)	$\delta^{13}C$ (C_3H_8)	δD (CH_4)	$\delta^{15}N$ (N_2)	$\delta^{13}C$ (CO_2)
C-1	3760	*E2*	–36.9	–35.1	–31.4	–145	–6.7	–
M-1	3930	*E2*	–34.6	–34.6	–31.3	–142	–7.4	–7.8

PETROGRAPHIC CHARACTERISTIC

The diagenetic history of carbonates of the Modryń formation is complex and includes minor, early marine cementation, several stages of dolomitization in shallow to moderately deep burial settings, and rapid as well as relatively long continuous episodes of fracturing (Zywiecki 1997). Oil migration and its transformation into gas took place in the burial diagenetic environments (Fig. 2).

The four types of calcite cements (CCI, CCII, CCIII and CCIV), and four types of saddle dolomite cements (SDI, SDII, SDIII and SDIV) were then generated as by-products of oil oxidation, fermentation and cracking into gas (*see* Zywiecki 1999). Anhydrite cements, elemental sulfur, sulfides, solid bitumens (pyrobitumens) and gas in the deposit were also products of the above mentioned processes. All the carbonate crystal accumulations on that stage grew inside fractures, caverns and intercrystalline pore spaces.

GAS GENERATION PROCESSES

The first oil migration took place during progressive burial of the source Famennian limestones and claystones of Bychawa formation capping porous Modryń formation carbonates. Due to the syn-depositional extensional Famennian faulting process (Zywiecki, Poprawa 2002), both source and reservoir rock formations came into contact one with another, what resulted in the lateral oil migration. Source rocks were buried to more then 2 km depth, and liquid hydrocarbons were probably generated during 10 mln years of the whole Famennian age.

The earliest oil migration occurred in the direction to north-east from south-west (Figs. 2, 3A). The first calcite cement (CCI) having negative $\delta^{13}C$ to −14.47‰ (PDB) only in the south-western field part (Fig. 3A), precipitated due to the bacterial oil oxidation processes:

2) C_5H_9 (oil) + $2FeOOH + 7O_2 + H_2O \Rightarrow 2Fe^{2+} + 5HCO_3^- + 4H_2O$,

with next decrease of bicarbonate concentration:

3) $HCO_3^- + 8H^+ \Rightarrow CH_4 + 2H_2O + OH^-$ (Irwin 1980),

and finally during pH increase due to methane production:

4) $Ca^{2+} + 2HCO_3^- + 8H \Rightarrow CH_4 + CaCO_3 + 3H_2O$ (Irwin 1980).

Next the process of oxidation of sulfur that was present in oil occurred in two stages:

5) $S^o + O_2 + H_2O \Rightarrow H_2SO_3$

6) $SO_3^{2-} + H_2O \Rightarrow SO_4^{2-} + 2e^- + 2H^+$ (Suzuki *et al*. 1994).

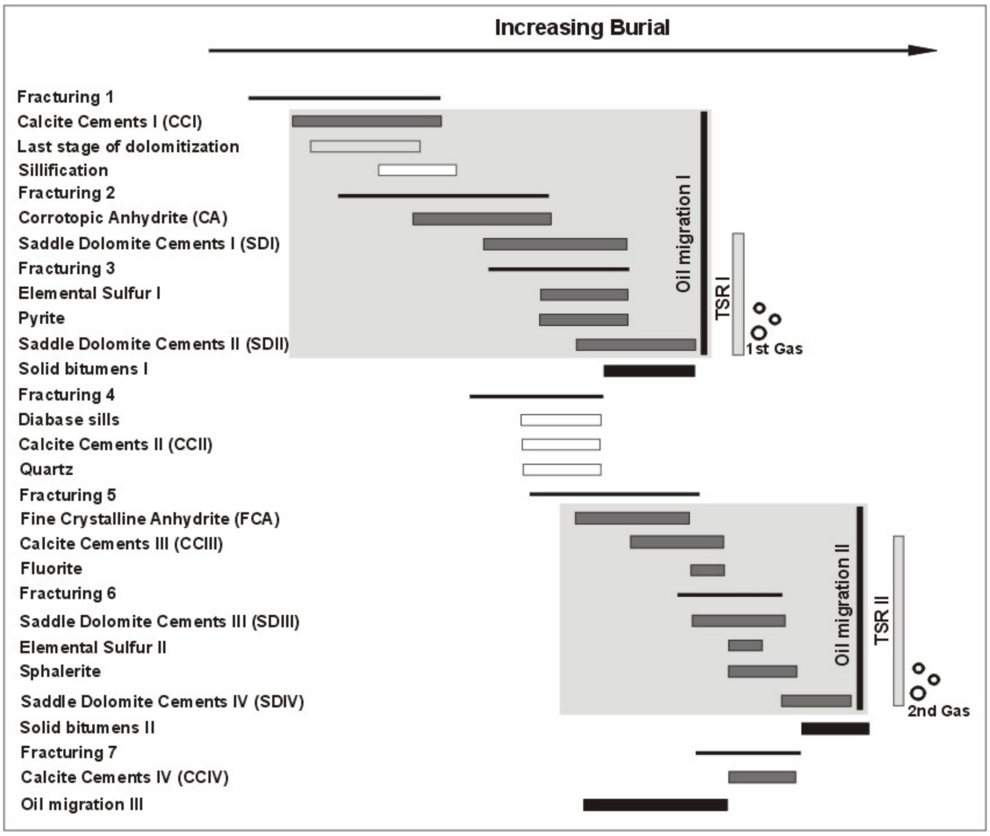

Fig. 2. Schematic diagenetic sequence of burial environments for the reservoir carbonates of Ciecierzyn-Mełgiew gas field. Overlapping episodes are listed according to the first appearance of their products.

This oxidation was stimulated by the presence of *Thiobacillus novellus* bacteria with sulfur-oxidizing enzyme, and produced equant (EA) and corrotopic (CA) anhydrite crystals (Fig. 2; Table 2) with $\delta^{34}S$ of + 23.1 to + 25.8‰ (CDT). The oxidation of sulfur from oil can occur in the presence of bacterial enzymes active simultaneously with Fe^{3+} as a catalyst agent. Sufficiently high contents of Fe and other heavy metals increasing oxidation potential, could be delivered by silicon-bearing fluids during oil emplacement (*see* Fig. 2: hydrothermal processes probably connected with diabase sills formation). Such influence was observed in hydrologic systems of various petroleum basins (*see e.g.* Parnell 1994).

7) $FeS_2 + 14Fe^{3+} + 8H_2O \Rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$ (Taylor *et al.* 1984)

8) $Ca^{2+} + SO_4^{2-} \Rightarrow CaSO_4$.

Table 2. Stable sulfur isotope composition of the evaporite and late anhydrites, euhedral pyrite and elemental sulfur.

Mineral type	$\delta^{34}S$ (CDT)	Well	Depth (m)	Unit
Evaporite anhydrites:				
- chicken wire nodules	+20.1	C-1	3672.3	*E3*
	+27.4	M-1	3917.6	*E2*
- relics of gypsum crystals	+22.4	C-9	3764.7	*E2*
	+16.8	M-4K	4031.8	*E2*
Late anhydrites:				
- equant crystals (EA)	+25.2	C-1	3792.7	*E2*
	+27.2	M-2	4280.3	*D2*
- corrotopic crystals (CA)	+23.1	C-5	3969.9	*D2*
	+23.7	C-6	3875.4	*E2*
	+24.8	M-4K	4077.7	*E2*
- fine crystalline concretions (FCA)	+29.5	C-5	3886.2	*E2*
	+32.9	M-4K	4052.8	*E2*
Euhedral pyrite	+20.3	C-3	3495.8	*F1*
Elemental sulfur	+22.8	C-4	3726.6	*E3*
	+30.3	K-1	3965.6	*E2*

Progressive burial (Fig. 2) caused the first thermochemical sulfate reduction (TSR I) and anhydrites were replaced by the first saddle dolomite cements (SDI; *cf.* Figs. 2, 3A):

9) $2Ca^{2+} + 2Mg^{2+} + 4SO_4^{2-} + 2C_2H_6 \Rightarrow 2CaMg(CO_3)_2 + 2H_2S + 2S + 4H_2O$.

Very high content of the light carbon isotope, yielding values of $\delta^{13}C$ of −19.37‰ (PDB) of SDI, occurred when precipitated pyrite with $\delta^{34}S$ of +20.3‰ (CDT), and elemental sulfur with $\delta^{34}S$ of +22.8‰ (CDT). This confirms the TSR I process (Figs. 2, 3A, Table 2):

10) $3H_2S + 2FeOOH \Rightarrow 2FeS + S^o + 4H_2O$

11) $FeS + S^o \Rightarrow Fe_3S_4 + 2S^o \Rightarrow 3FeS_2$ (equation summary from Prosser *et al.* 1994).

Next process of oil fermentation caused the growth of the second saddle dolomite cements (SDII; *cf.* Figs. 2, 3B) with high fraction of the heavy carbon isotope yielding values $\delta^{13}C$ = +7.67‰ (PDB):

12) $CO_2 + H_2O \Rightarrow H_2CO_3 \Rightarrow H^+ + HCO_3^-$ (Irwin 1980),

13) $Ca^{2+} + Mg^{2+} + 2HCO_3^- \Rightarrow CaMg(CO_3)_2 + 2H^+$.

The extensive growth of carbonate (calcite and dolomite) cements could be additionally connected by the delivery of SO_4^{2-} from oxidation of sulfur and/or sulfides. This process caused the increase of acidity and dissolution of host rock calcite and dolomite enriching solutions in Ca^{2+} and Mg^{2+}. Further decrease of acidity led to carbonate precipitation.

Final cracking of oil into gas produced the methane accumulation and the first solid bitumens (pyrobitumens; *see* Hunt 1996) as a by-product (Figs. 2, 3B):

14) C_5H_9 (oil) $\Rightarrow 2CH_4$ (gas) $+ C_3H$ (pyrobitumen).

This process developed in western field area before the uplift of the central Lublin basin in the Late Visean (Figs. 1, 2), as evidenced by the presence of the first calcite cements (CCI) and the first solid bitumens (SBI) in clasts of the Frasnian sedimentary rocks in the Late

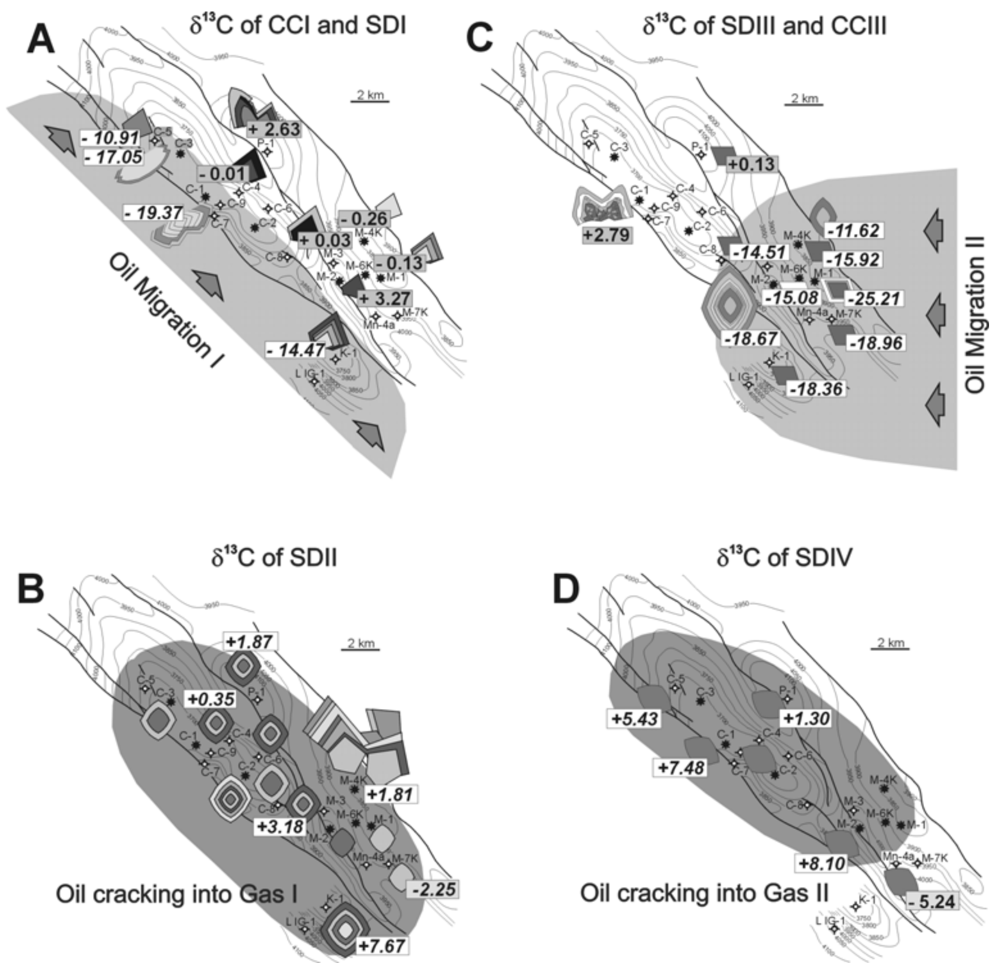

Fig. 3. (A) North-eastern direction of the first oil migration evidenced by carbon stable isotope record of calcite and saddle dolomite cements (CCI and SDI), indicating oil oxidation process. (B) Thermal maturation and cracking into the first gas recorded by stable carbon isotopes in saddle dolomites (SDII). (C) Western direction of the second oil migration evidenced by carbon stable isotope record of the calcite and saddle dolomite cements (SDIII and CCIII), indicating a subsequent oil oxidation process. (D) Thermal maturation and cracking into the second gas noticed by stable carbon isotopes in saddle dolomites (SDIV). Compare to Fig. 2.

Visean alluvial fans. The solid bitumens from the described gas field show no algal or organic compound particles, vitrinite, and macerals in UV light fluorescence. Reflectance of the observed solid bitumens exceeds 3.0 % and indicates impsonite phase, a form of organic compound typical of gas occurrences.

The second time oil migrated during next burial of the Famennian beds from the early Late Carboniferous to about Early Permian (Fig. 2), while Lublin basin area was affected by strike-slip movements (*see* Zywiecki, Poprawa 2002). This time liquid hydrocarbons were expulsed from eastern direction (Fig. 3C), causing the crystallization of inorganic structures in the style like that which yielded from the first oil migration and maturation (Fig. 2). Fine crystalline anhydrites (FCA, *cf*. Fig. 2 and Tab. 2) with δ^{34}S of +29.5 to

+32.9‰ (CDT), indicate "closed system". These values are due to sulfur and sulfate origin from oil bacterial oxidation. The second thermochemical sulfate reduction (TSR II) involved precipitation of the third saddle dolomite cements (Fig. 2) with $\delta^{13}C$ of −18.67‰ (PDB), and additionally the third calcite cements (Figure 2, 3C):

15) $CaSO_4 + 3H_2S + CO_2 => CaCO_3 + 4S^o + 3H_2O$ (Worden *et al.* 1995)

with $\delta^{13}C$ of −25.21‰ (PDB), and elemental sulfur (Fig. 2; Tab. 2) with $\delta^{34}S$ +30.9‰ (CDT) values. The following oil bacterial fermentation formed the fourth saddle dolomite cements (SDIV; *see* Fig. 2) with $\delta^{13}C$ +8.10‰ (PDB) values. The last final cracking of oil into gas produced high-methane medium with the second solid bitumens (SBII, in fact pyrobitumens) as a by-product, which is concentrated mainly in the eastern field area (Figs. 2, 3D).

CONCLUSIONS

Petrographic and isotope analysis of diagenetic inorganic products in the carbonate reservoir rocks of the Devonian age in Lublin basin resulted in the opportunity to trace in details the stages of chemical processes during oil charging into the reservoir area and formation of economic gas accumulation.

Two episodes of oil migration, oil bacterial oxidation, thermochemical sulphate reduction, oil bacterial fermentation and oil cracking into gas were responsible for the observed sequence of the growth of the diagenetic minerals and gas field formation. Significant role of bacterial activity on almost all diagenetic stages, even of a relatively deep burial setting, was recognised. Two source rock sub-basins surrounding the final gas field area delivered oil to the reservoir rocks in two episodes in different time during subsequent stages of strike-slip tectonic movement of the basin.

Thus, the Lublin basin area should be explored for hydrocarbon accumulation by investigating the history of Late Devonian, Carboniferous and Permian extensional and wrench tectonics, and understanding of facial and structural stage development of the source and reservoir rocks connections with events of paleoburial conditions of hydrocarbon generation and migration. Block-style of pull-apart Lublin basin development would caused recent absence of the source rocks due to late Carboniferous and Permian erosion of some areas, which, however, gave to the system large amounts of hydrocarbons during Variscan time.

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