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HYDROCARBON COMPOUNDS AND PLAUSIBLE MECHANISM OF GAS GENERATION IN "SHALE" GAS PROSPECTIVE SILURIAN DEPOSITS OF LVIV PALEOZOIC DEPRESSION

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Purpose. Investigations of composition of gas within closed porosity (fluid inclusions and closed pores in rocks) of prospective gas-bearing Silurian graptolitic argillites of Lviv Paleozoic depression and ground of plausible mechanism and dynamics of gas generation during "shale" gas formation in productive strata of black-shale formations of the region. **Methodology.** The composition of volatile of fluid inclusions and closed pores of rocks, and their relative gas saturation and water saturation were determined by mass spectrometric chemical method. Inclusions and closed pores were opened by crushing a standard sample (sample weight 200 mg, +1-2 mm fraction) in a small metal cylindrical mortar between two plane-parallel hard carbide alloy (pobedit) surfaces in high vacuum (approx. 1×10^{-3} Pa). **Results.** According to data for mineral-fluidological research, methane prevails (up to 100 vol.%) with minor content of ethane, carbon dioxide and nitrogen in gas phase of fluid inclusions and closed pores of Silurian graptolitic argillites of Lviv Paleozoic depression. Lack of the steam may indicate "dryness" of hydrocarbon-bearing systems, and low values of relative gas saturation – the conversion of organic matter as a source of volatile hydrocarbon compounds at the low (mainly, litostatic) pressures. This indicates the reality of passage of processes of gas production during the transformation of organic matter of argillite strata. Higher by one order the relative gas saturation of inclusions in calcite, which healed subvertical fractures in argillites, had the appearance of the steam indicates the likely influx of deep-seated migrating fluids via powerful crack systems. It was grounded that the plausible mechanism and dynamics of gas generation followed by capture of gas in free state and sorption and occlusion within rocks, intensified by influence of deep-seated fluids. It is based on a comparison of data on the composition of volatile compounds of fluid inclusions and closed pores of prospective gas-bearing argillites and sorption-generation processes of methane generation in coal, based on the principle of unity of nature of transformation of dispersed and concentrated form of organic matter. **Originality.** For the first time relics of renewable, almost substantially hydrocarbon anhydrous (dry) fluids in fluid inclusions and closed pores (cavities, cracks) of shale gas prospective graptolitic argillites of the Paleozoic of the Volyn-Podillya there were found. This indicates the presence geo-fluid-dynamic conditions, both for the generation of hydrocarbons in the conversion of organic matter, absorbed and occluded by mineral and organic component of rocks at the stage of katagenesis, and the influx of deep-seated hydrocarbon fluids, and thus confirms shale gas potential of mineral resources of the region. **Practical significance.** The influence of volatile compounds in closed porosity (fluid inclusions and closed pores of host rocks (graptolitic argillites)) for the total gas-bearing potential of shale-bearing strata is estimated, which will be significant, regardless of other aspects of the problem (especially social and environmental issues), for the eventual estimate of shale gas resources (reserves).

Keywords: volatile; fluid inclusions; closed pores; "shale" gas; graptolitic argillites; Silurian; Lviv Paleozoic depression.

Introduction

Recently, the prospects of gas-bearing potential of Lviv Palaeozoic depression have been associated, primarily, with the discovery of deposits of "shale" gas [Lukin, $2010_{1,2}$; Kurovets' et al., 2010, 2012; Loktyev et al., 2011; Hubych et al., 2012].

However, the discussed risks [Loktyev et al., 2011; Kharkevych, Misyura, 2011; Pavlyuk et al., 2013; Kurovets' et al., 2014; Naumko et al., 2015] call for a balanced approach to the assessment of its occurring within rocks. Therefore, the study of composition of fluids and dynamics of geochemical processes during the formation of prospective gas-bearing complexes is one of the top priority tasks within the outlined problem.

Given the particularity of "shale" gas as a discrete gas phase, on the one hand, absorbed by mineral and organic matter, on the other hand – occluded by defects of closed porosity of rocks (fluid inclusions, closed pores, travelling rugs, cavities, cracks), special importance is attached to the identification of hydrocarbon compounds in them and justification of plausible mechanism for gas generation. This will promote establishing its content and features of the spatial distribution in the productive strata of black-shale formations in the region as a prerequisite of creating a methodological base for "shale" gas resources (reserves) estimate.

What differs in this study from the existing literature data on the content and composition of the gas in shale gas- prospective strata [Stavyts'kyi, Holub, 2011; Hubych et al., 2012; Zagnitko, Mykhailov, 2014; Mykhailov et al., 2014], is the use of techniques of thermobarogeochemistry-mineralofluidology [Kalyuzhnyi, 1982], in particular, the method of mass-spectrometric chemical analysis of volatile components of closed porosity (fluid inclusions and closed pores in rocks) of gas-bearing prospective sections. A characteristic feature in this technique is the release of volatile from fluid inclusions and closed pores by mechanically grinding rock samples which resembles the conditions of rock crushing in the area of artificial hydraulic fracturing (fracking).

We studied rocks of Lishchyna (parametric well 1-Lishchynska) and West Buchach (parametric well 3-Buchach) structures of Lviv Palaeozoic depression, primarily because of the prospects of the Silurian strata being rich in shale gas, as well as the likelihood of discovering of new gas fields in the Devonian sediments and new complex gas-coal deposits in the Carbon sediments [Lyzun et al., 2001] due to vertical migration inflow of methane from underlying rock complexes [Zinchuk et al., 2003; Naumko, 2006; Pavlyuk et al., 2008].

Purpose

Investigation of gas composition within closed porosity (fluid inclusions in minerals and closed pores in graptolitic argillites of prospective gas-bearing Silurian sediments of the Lviv Paleozoic depression and justification of the probable mechanism and dynamics of gas generation during shale gas formation in productive strata of black-shale formations was carrie out in the region.

Methodology

The composition of volatile fluid inclusions and closed pores in graptolitic argillites, and their relative gas saturation (increase of pressure in the assumed system of a mass-spectrometer relative to its residual value of the order of $1 \cdot 10^{-3}$Pa grinding chamber (ΔP), Pa) and water saturation (content of the steam (absorber – P_2O_5) in total volume of volatile (C_{H2O}), vol.%) were determined by mass- spectrometric chemical method using time-of-flight mass-spectrometer MCX-3 (1–200 atomic unit of mass).

Inclusions in minerals and closed pores in rocks were opened by crushing the standard sample (weight 200 mg, +1-2 mm fraction) in a small metal cylindrical mortar between two plane-parallel hard carbide alloy (pobedit) surfaces in high vacuum (approx. 1×10^{-3} Pa).

Area of study

Prospective “shale” gas-bearing rock complexes [Poprava, 2009; Kurovets' et al., 2010; Loktyev et al., 2011] are considerably spread within the south-western margin of the East European platform, in particular in the Teysseyre-Tornquist Zone (or the Transeuropean suture zone), including within Ukraine (Fig. 1). They are represented by deep-sea terrigenous sediments, mainly graptolitic argillites of Lower Paleozoic [Einasto et al., 1980; Dryhant, 2000]. Across continuous sequence of Sylurian – Lower Devonian strata are characterised by almost sub-meridional directionality of clearly marked facial zones and significant increase of the thickness of stratons westward. It lies on top of Ordovician, Cambrian and Vendian surfaces were eroded during prolonged regression (caused by Takon orogeny phase).

Richness of these strata in organic matter allows us to consider them as gas-forming strata [Poprava, 2009].

A representative section of deep-sea terrigenous sediments of the Silurian in the Lviv Paleozoic depression is provided by a parametric well 1-Lishchynska.

Results of study

Our research of Silurian graptolitic argillites, in particular, on the material of core from the parametric well 1-Lishchynska (Int. 2278–3537 m) [Kurovets' et al., 2010, 2012] showed.

These rocks are typical black massive argillites rich in organic matter (Fig. 2) and split by multiple subvertical, more rarely horizontal cracks healed predominantly with calcite (Fig. 3).

The results of petrophysical laboratory studies found that this argillite's open porosity varies within 0.6–2.4 % and it is almost impermeable (less than 0.001 $\mu m^2 \cdot 10^{-3}$). The content of carbonate material reaches 20 %. The lowest volume density (2.64–2.70 g/cm^3) is characteristic for argillites with coalised organic substance and the highest (2.75–2.8 g/cm^3) – for massive hydromica argillites with inclusions of the pyrite.

According to the thermal analysis of 21 samples it was found that the content of TOC (total organic carbon) ranged from 0.75 to 2.38 %.

Chemical analysis made it possible to establish that the content of silica is on average 50 % regardless of its depth.

The samples after crushing in a sieved well which, along with these data, show the prevalence of silica component over clay component, which will likely favour fracking phenomena.

According to [Dmitrievskiy et al., 2011] the main criteria of bituminous shale gas-bearing prospects should include the following:

– the amount of organic matter exceed one percent to generate industrial-grade gas accumulations;

– the degree of maturity of organic matter by vitrinite reflectance (VR) (R_0) should be recorded in values over one which favours mass generation of gas hydrocarbons – the main zone of gas production;

– the content of clay material shall not exceed 50 %, otherwise the layer will plastically deform and will not be able to develop cracks gas migration ways.

Overall, deposits of Volyn-Podillya satisfy the above listed criteria of shale gas prospectiveness [Kurovets' et al., 2010; Loktyev et al., 2011; Kurovets' et al., 2012, Hubych et al., 2012; Kurovets' et al., 2014], which is consistent with data on the adjacent territory of Poland [Poprava, 2009]. Therefore, the primary task of the present stage of a study in the region is seen to establish the presence of hydrocarbons in a closed pore space of graptolite argillite (fluid inclusions in minerals and closed pores of rocks) which allows us to get valuable data about the gas-bearing prospects of the studied sections with regard to content and peculiarities of the spatial distribution of shale gas in them [Naumko et al., 2012].

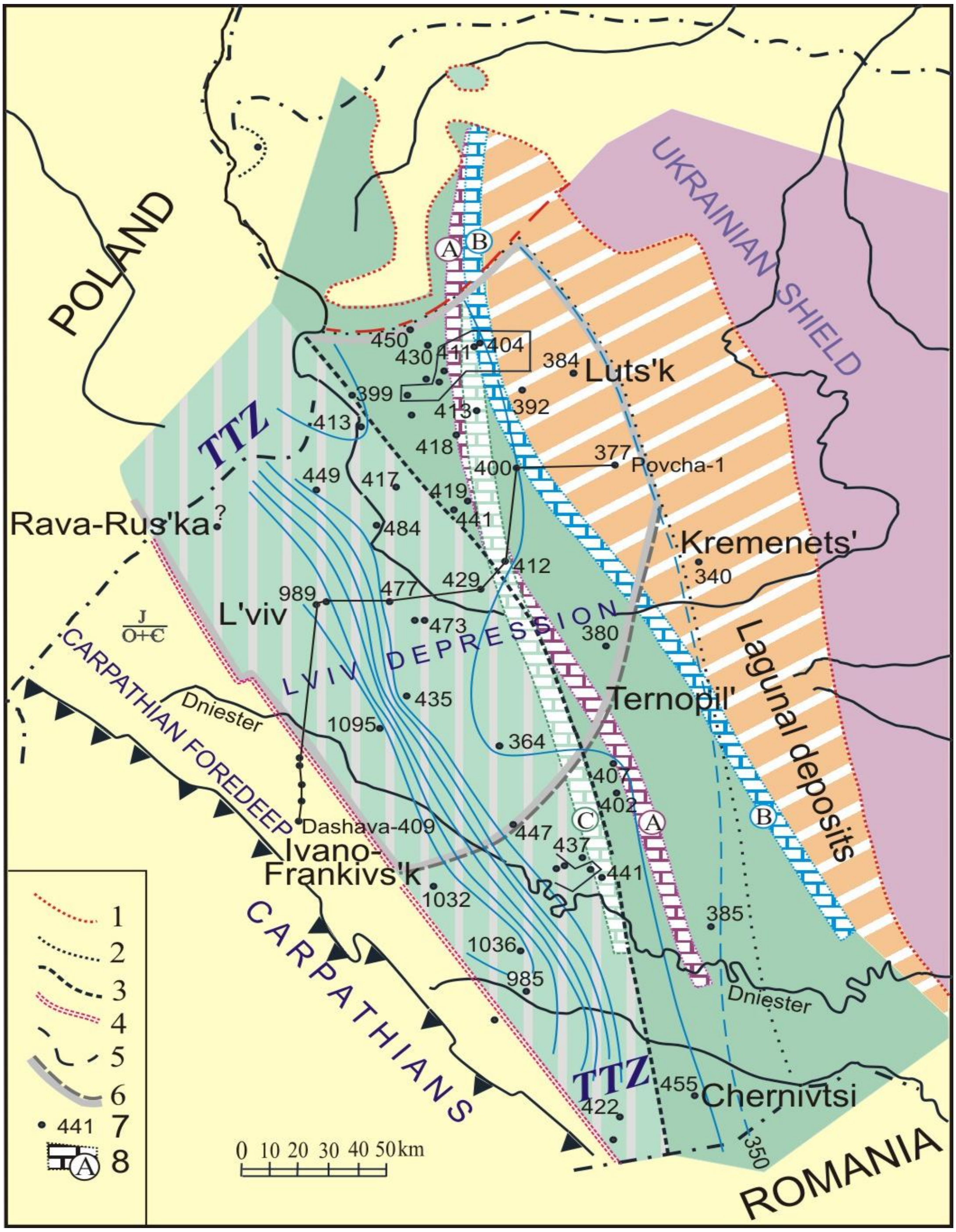


Fig. 1. *Scheme of spreading and isopach map of the Silurian deposits [Kurovets' et al., 2012]:*
1 – Eastern extend of the Silurian deposits; 2, 3 – Eastern extend of the Lower Devonian deposits; (2 – Tyver Superhorizon, 3 – Dniester Series); 4 – Western extend of the Silurian deposits; 5 – fault; 6 – Lviv Depression limits; 7 – boreholes and thickness; 8 – extend of the biohermic barriers (A – Bagovytsya, B – Konivka, C – Isakivtsi suite); TTZ – Teisseyre-Tornquist Zone

Fig. 2. *Shows the typical appearance of Silurian black massive graptolitic argillites enriched with organic matter in core for the section of the parametric well 1-Lishchynska: sample Lishch. 1-66, depth interval 3450–3454 m, core – 78 mm*

As determined by mass-spectrometric chemical analysis, within volatile components of fluid inclusions in minerals and closed pores (cavities, cracks) in graptolitic argillites, which are linked to the "shale" gas as a discrete gas phase, the section of well 1-Lishchynska is dominated by methane (up to 100 vol.% in the depth interval 2750–2755, 2800–2804 and 2998–3003 m), but in deeper (intervals 3402–3406 and 3500–3504 m) methane content decreases (79.2 to 62.1 vol.%,). The concentration of carbon dioxide increases (3.9 to 12.0 vol.%) and nitrogen increases (11.5 to 25.9 vol.%). It is also important to note that ethane appears (5.4 vol.%) (Table. 1, Fig. 4).

Attention is drawn to the absence of the steam, which may indicate "dryness" of fluid systems present in argillite stratum.

The total mass concentration of components ($12.440–61.600 \cdot 10^{-6}$ g/g sample) is very high. In order to determine it, a chopped analyzed sample was sieved through a 0.25 mm sieve and results were attributed to the sifted part of the sample. Since the vacuumation of graptolitic argillites samples was slower compared to other samples of rocks, and degassing in the vacuum continued after the analysis, the content of natural gas is probably higher.

Note that within the influence of artificial hydraulic fracturing, rock under powerful hydrodynamic impact can be broken down to even smaller particles. Since by disclosure of pores of smaller volume (reaching down to perhaps nanoscale [Kiriukov et al., 2009], at the level of minerals structure) the concentration of volatile components will increase, and the amount of gas that can be extracted from rocks will probably reach even higher values.

Low values of relative gas saturation in host graptolitic argillites (0.08–0.27 Pa) confirm the traditional idea that the source of the volatile compounds of "shale" gas (primarily hydrocarbon compounds) is organic matter, which conversion took place at low mainly, litostatic pressures.

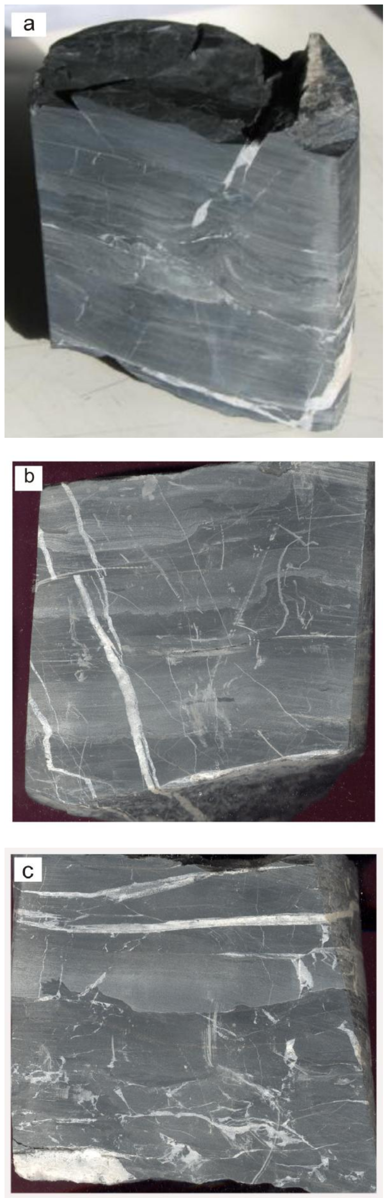


Fig. 3. *General view of the core with vertical (subvertical) (a, b) and horizontal (c) cracks in Silurian graptolitic argillites healed calcite with formation veinlet-impregnated mineralization for the section of the parametric well 1-Lishchynska :*
a – sample Lishch. 1-44, depth interval 2800–2804 m, core – 78 mm;
b – sample Lishch. 1-48, depth interval 2800–2804 m, core – 78 mm;
c – sample Lishch. 1-46, depth interval 2800–2804 m, core – 78 mm

This is consistent with known findings by E. B. Chekaliuk [Chekaliuk, 1990], which were reached on the basis of thermodynamic calculations of marginal pressures of gas generation during the process of dehydration of organic matter in the Earth's crust.

The overall balance of “shale” gas in the world, however, is convincing evidence of the influx of deep hydrocarbon fluids from diverse sources [Dmitrievskiy et al., 2011], in particular dualistic abiogenic-biogenic sources [Naumko, 2006, 2015].

In our case it is confirmed by: isotopic composition of carbon of calcite veinlet-impregnated mineralization ($\delta^{13}S$=-3,88‰ (PDB), after etching with hydrochloric acid -8,34‰ [Zagnitko et al., 2011; Mykhailov et al., 2014]); essentially methane volatile substance composition (100 vol.%); by one order higher relative gas saturation (1.07 Pa) compared with holding argillite (0.07–0.27 Pa); the presence of water vapor within inclusions in calcite (see Table 1) which healed powerful systems of interconnected migrational subvertical and horizontal cracks in argillite strata (see Fig. 3).

Therefore, in fluid inclusions in minerals and closed pores (cavities, cracks) in graptolitic argillites we found relics of renewable, almost substantially hydrocarbon anhydrous (“dry”) fluids as a crucial prerequisite for the formation of deposits of “shale” gas.

Similar numbers are as well characteristic for section of the parametric well 3-Buchach [Naumko et al., 2009] (see Table 2 and, Fig. 4).

Note that the comparable data available in the literature, with regards both to Volyn-Podillya and other regions, mention a somewhat wider range of identified hydrocarbon compounds [Stavyts'kyi, Holub, 2011; Hubych et al., 2012; Zagnitko, Mykhailov, 2014; Mykhailov et al., 2014], which can be explained by the use of other methodological approaches to extraction and analysis of volatile.

The plausible mechanism of the formation of “shale” gas

Based on the analysis obtained author data by means of chemical mass-spectrometry on composition of volatile compounds (see. Tables. 1, 2, and Fig. 4) and materials [Stavyts'kyi, Holub, 2011; Hubych et al., 2012; Zagnitko, Mykhailov, 2014; Mykhailov et al., 2014] with an attraction of literary information on methane sorption-generation processes in coal [Kiriukov et al., 2009; Khramov, Lyubchak, 2009] we substantiated plausible mechanism and dynamics of gas-generation and origin of “shale” gas.

Table 1

Composition of volatile of fluid inclusions and closed pores in rocks for the section of the parametric well 1-Lishchynska in the Lviv Palaeozoic depression (according by data of mass-spectrometric chemical analysis[1])

Sample number	Depth (interval) of the selection, m	Rock, mineral	Components[2]: Voluminous particle,% / Mass concentration, $n\times10^{-6}$ g/g of sample				Relative gas saturation Δ P, Pa[3]	Water saturation C_{H2O}, vol.%[4]	Total mass concent., $n\times10^{-6}$ g/g of sample[5]
			CO_2	N_2	CH_4	C_2H_6			
Lishch. 1-39	2750–2755	Argillite	–	–	100.0 / 3.900	–	0.08	–	19.200
Lishch. 1-48	2800–2804	Argillite	–	–	100.0 / 61.600	–	0.27	–	61.600
Lishch. 1-48	Ibid	Calcite	–	–	100.0 / 49.360	–	1.07	8.5	49.360
Lishch. 1-56	2998–3003	Argillite	–	–	100.0 / 15.400	–	0.07	–	15.400
Lishch. 1-61	3402–3406	Argillite	3,9 / 0.233	11,5 / 1,333	79.2 / 40.333	5,4 / 0.333	0.16	–	42.232
Lishch. 1-69	3500–3504	Argillite	12.0 / 0.800	25,9 / 2,600	62.1 / 9.000	–	0.10	–	12.400

Notes:

[1] analyst B. E. Sakhno (mass-spectrometer MCX-3A);

[2] sample of the mineral (rock) weight of 200 mg fraction + 1-2 was crushed by squashing in a specially designed mortar, before the analysis, the assumed system of the mass-spectrometer was vacuumed to values of order 1×10^{-3} Pa;

[3] relative gas saturation Δ P, Pa – the increase of pressure in the assumed system of the mass spectrometer (with respect to the residual pressure of order 1×10^{-3} Pa in it), which is created as a result of the release of volatile components (without taking into account the steam, sorbed on P_2O_5, placed in the assumed system) from inclusions and closed pores in the chopping of the sample and may be a comparative value for the same weight;

[4] relative water saturation C_{H2O}, vol.% – percentage of the steam, that was absorbed on P_2O_5 placed in the assumed system, in the total volume of released volatile components;

[5] to determine the mass concentration of the crushed and analyzed sample was sifted through a 0.25 mm sieve and the results were attributed to the sieved portion of the sample.

Table 2

Materials to the consolidated characteristic of complex reservoir-rocks for the section of the parametric well 3-Buchach in the Lviv Palaeozoic depression

Sample number	Depth of (interval) of selection, m	Lithology	Age	Reservoir properties of rocks				Fluid inclusion in minerals and closed pores of rocks (according to chemical mass spectrometry[1])					
				Open porosity, under normal conditions K_p^o,%	Permeability at the Kerosene, $K_{per.}$, m^2 ×10^{-15}	Volume density, ρ, g/cm^3	Carbo-nation, C,%	Composition of volatile components, vol.%[2]				Relative gas saturationΔ *P*, Pa[3]	Water saturation C_{H2O}, vol.%[4]
								CO_2	N_2	CH_4	Ar		
Buch. 3-25	1000–1006	Limestone debris argillaceous	S	0.72	Impenetrable	2.70	42.0	0.5	–	99.5	–	0.63	–
Buch. 3-32	1028–1034	Limestone biomorphic with skeletal remains of trilobites	S	1.,02	Impenetrable	2.70	61.0	1.2	–	98.8	–	0.20	–
Buch. 3-32	Ibid	Secretions of calcite from limestone						–	–	100.0	–	0.57	+[5)]
Buch. 3-36	1051–1055	Limestone biomorphic conglomerate similar	S	0.78	Impenetrable	2.71	57.0	0.1	–	99.9	–	0.75	+
Buch. 3-39	1080–1084	Limestone organogenic-debris	S	0.62	0,027	2.71	44.0	0.7	–	99.3	–	0.40	–
Buch. 3-46	1151–1157	Limestone debris argillaceous	S	0.58	Impenetrable	2.73	48.0	0.9	–	99.1	–	0.23	–
Buch. 3-71	1453–1457	Sandstone quartz fine-grained	Є	1.46	0.00015	2.66	3.0	11.2	–	88.8	–	0.13	–
Buch. 3-91	1731–1736	Sandstone quartz	Є	6.55	0.0021	2.52	3.0	8.9	2.1	89.0	–	0.07	–
Buch. 3-115	2101–2106	Arkose	PR_3	2.64	Impenetrable	2.71	0,0	13.4	46.7	39.9	–	0.08	+
Buch. 3-115a	Ibid	Arkose changed	PR_3		Impenetrable			59.2	19.4	21.1	0,3	0.40	67.5
Buch. 3-116	2159–2153	Bark of weathering of acid rocks	AR +PR	3.02	Impenetrable	2.63	2.0	–	85.4	14.6	–	0.27	70.4
Buch. 3-117	2208–2213	Granite hornblende	AR +PR	2.58	Impene-trable	2.64	1.0	–	80.1	18.8	1,1	0.23	65.2

Notes:

[1] analyst B. E. Sakhno (mass-spectrometer MCX-3A);

[2] sample of the mineral (rock) weight of 200 mg fraction + 1-2 was crushed by squashing in a specially designed mortar, before the analysis, the assumed system of the mass-spectrometer was vacuumed to values of order $1\cdot10^{-3}$ Pa;

[3] relative gas saturation Δ P, Pa – the increase of pressure in the assumed system of the mass spectrometer (with respect to the residual pressure of order $1\cdot10^{-3}$ Pa in it), which is created as a result of the release of volatile components (without taking into account the steam, sorbed on P_2O_5, placed in the assumed system) from inclusions and closed pores in the chopping of the sample and may be a comparative value for the same weight;

[4] relative water saturation C_{H2O}, vol.% – percentage of the steam, that was absorbed on P_2O_5 placed in the assumed system, in the total volume of released volatile components;

[5] probably the steam is present.

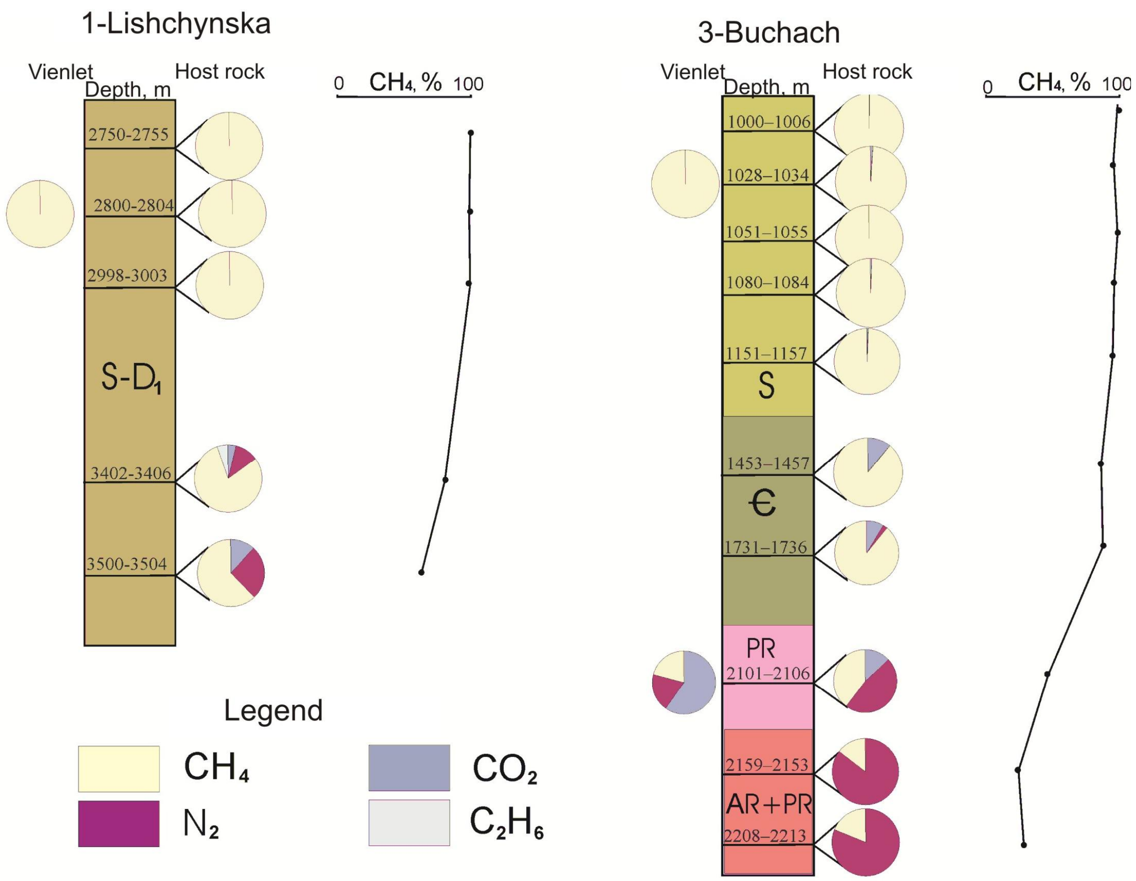


***Fig. 4.** Change of the composition of volatile of fluid inclusions and closed pores in rocks for the sections of parametric wells*
1 – Lishchynska and Buchach in the Lviv Palaeozoic depression (according by data of mass-spectrometric chemical analysis (see Tables 1, 2))

We proceed from the principle of unity of nature and ways of transformation of dispersed (in this case in the form of the kerogen in argillites) or concentrated (as in coal) as forms of organic matter [Geologicheskiy slovar', 2012], considering that studied graptolitic argillites and coal differ only in the amount of organic matter, scattered in the form of kerogen in argillite or concentrated in coal [Naumko et al., 2013].

According to scanning electron microscopy [Kiriukov et al., 2009] it was found that sorption and generation of methane in coal occurs simultaneously in several stages (Fig. 5):

1) initial methane generation – isolation of CH_3 radicals from initial matrixof coal and its frame and formation of CH_4 molecules;

2) methane sorption – formation of an equilibrium system “sorbate (modified coal matrix and its frame – sorbent (methane molecules)”;

3) desorption – the destruction of the “sorbate-sorbent” system;

4) filtration of separated gas – its transfer through the porous surrounding environment.

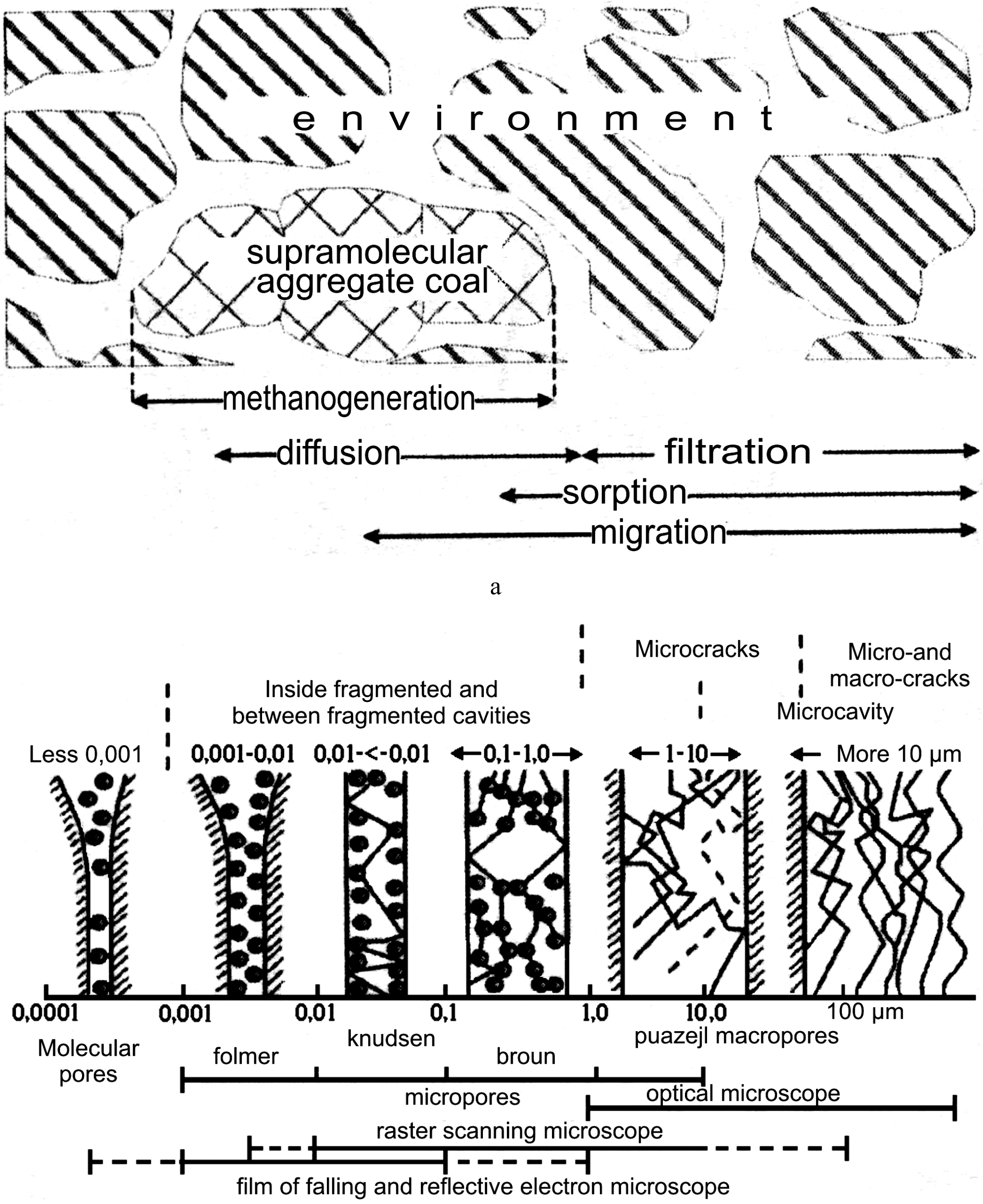
Accordingly justified from the standpoint of classical molecular physics and the colloid chemistry mechanism [Khramov, Lyubchak, 2009] methane generation in the porous space of coal passes on the decomposition of macromolecular organic matter as a result of chain free-radical reactions of methyl radical in the pore space of lito-basis which is characterised by increasing volume and local manifestations of high degree of the rarefaction created by the combination of nano-, micro- and macrostructures in heterogeneous system gas-(finely grinded) coal (Fig. 6, 7).

Extrapolating data from studies of methane sorption and generation processes in micro- and nanostructures of coal [Kiriukov et al., 2009; Khramov, Lyubchak, 2009] on conversion of organic matter of prospective gas-bearing complexes and complementing them with our data we can suggest a plausible mechanism of gas generation in the pore space of rocks followed by occlusion of free state gas into fluid inclusions in minerals and closed pores, cavities and cracks, and in the same way absorbed by kerogen already strictly as “shale” gas.

At the beginning of the transformation of sedimentary strata under quiet geodynamic conditions within buried organic matter there happen slow restructuring changes and, consequently, chemical changes in the direction of carbonization during which both methane (CH_4) and free radicals, especially CH_3 (to formation of ethane (C_2H_6) and other hydrocarbons) are formed – in the process of diagenesis ***biogenic*** gas in the upper zone of gas-generation is formed.

Later at appropriate stages of katagenesis during rock thermodestruction under conditions of increased temperature and pressure, structural changes of organic matter intensify which favours increased gas generation and formation of ***thermobaric*** gas.

When the certain critical concentration of free radicals is reached, free-radical chain reactions [Zherebets'ka et al., 2011] are initiated. The condition for the creation of a critical concentration of free radicals is a sudden momentary unsettlement of the local dynamic equilibrium in the reservoir. This leads to appearance of ***newly-generated*** gas in pores, down to perhaps nanoscale-sized pores at the level of structure of minerals [Kiriukov et al., 2009].



b

Fig. 5. *Means of migration of coal methane [Kiriukov et al., 2009]:*

a – scheme of ratio migration methane in supramolecular aggregates and environment of standard coal; b – size and pore types, methods for assessing permeability and species migration of methane in fossil coal (A. T. Airuni and V. V. Kiryukov)

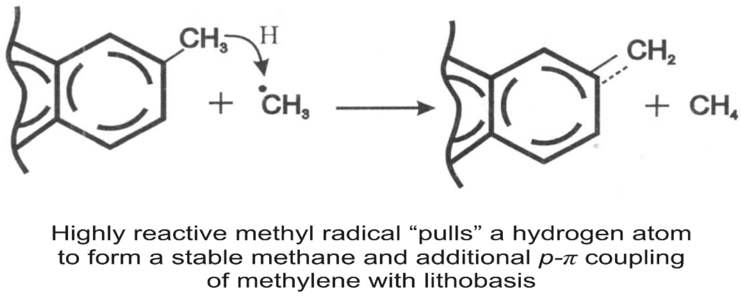


Fig. 6. *The chemical scheme of a homolytic reaction for example methyl radical [Khramov, Lyubchak, 2009]*

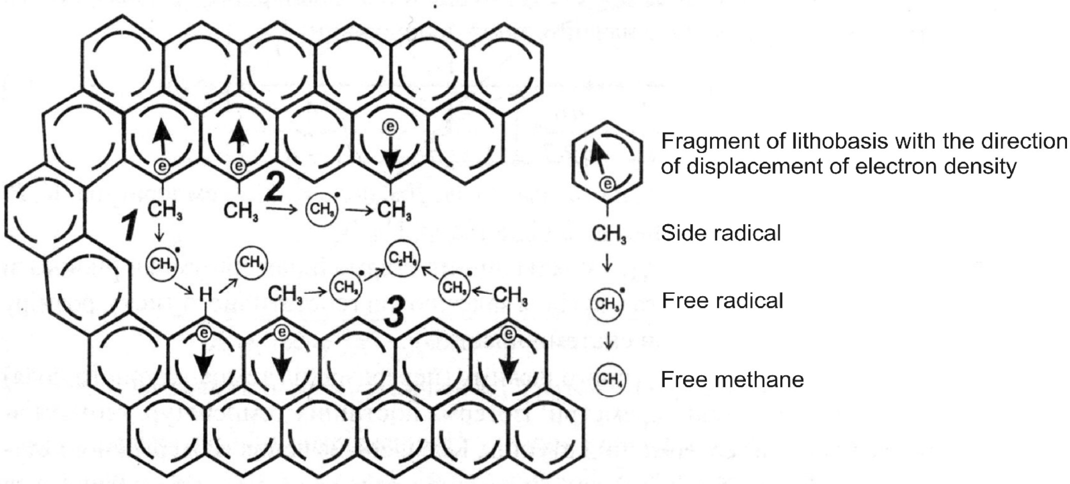


Fig. 7. *Mechanisms of chemical reactions of a methyl radical in the pore space of the lithobasis [Khramov, Lyubchak, 2009]*

The favorable factors include:

1) natural factor – hydrodynamic shock (for example transformation of seismic shock into hydraulic shock as is meant by V. P. Linetskiy [Linetskiy, 1974] or manifestations of the tectonic-dynamic destabilization [Solovjov, 1996, 2011]) in the area of introduction of deep-seated high-temperature fluid and corresponding inflow of ***deep-seated*** gas, in particular gas of abiogenic-biogenic origin [Naumko, 2006, 2015];

2) artificially created factor – hydrodynamic shock in the area of artificial hydraulic shock during hydraulic fracturing stimulation – ***stimulated*** gas generation.

Note that under the conditions of influence of deep fluids catalytic properties of clay minerals (Fig. 8) [Kosachev et al., 2010] are extremely enhanced, as a result of intensifying gas generation processes that were manifested in earlier stages of forming sedimentary strata under intense diagenetic formation of methane, and the adsorption of organic compounds by the surface of rock-forming minerals, with the appearance of hydrophobic properties of pore space of rocks both on micro- and macro-level that promotes permanent inflow of natural gas [Lukin, $2011_{1,2}$].

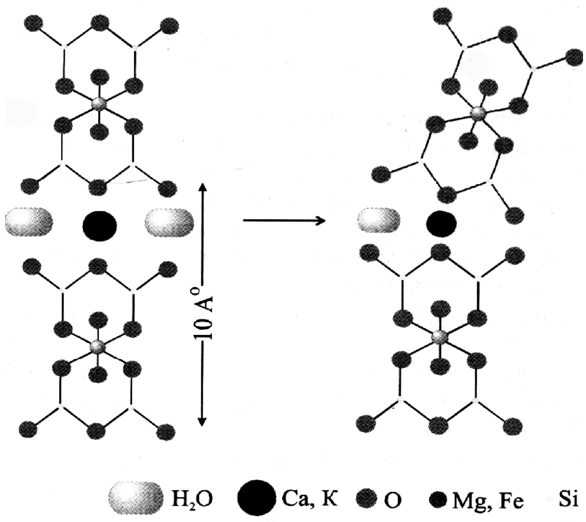


Fig. 8. *The scheme of structural transformation of clay minerals as a result of the partial removal of interlayer water molecules [Kosachev et al., 2010]*

The fact that the genesis of the majority of gases saturated with organic matter strata is associated with both processes of transformation and coalification of organic matter and, mainly, with their influx from endogenous cells both of crust and mantle nature, is confirmed by other researchers (for example [Zagnitko, Mykhailov, 2014]).

The study of "shale" strata of Volyn-Podillya along the section of the well 1-Lishchynska by the methods of EPR- and IR-spectroscopy [Bezruchko et al., 2015], showed that organic matter of rocks has relatively low absorption properties and negligible methane generation potential. It is insufficient the amount of organic matter is believed [Loktyev et al., 2011] to be the root cause of the lack of conventional fields in the sediments of the lower Paleozoic and limited displays of natural gas during drilling in the Lviv Palaeozoic depression. If one considers almost complete absence of positive results of exploration drilling [Orlov et al., 2013; Filipovich, Kudryashov, 2013] and ambiguity of "shale" gas reserve calculation [Mykhailov et al., 2014] within the Baltic, Podlaskie and Lublin basins, there is a negative factor of over-estimation of potential in the studied area, because "shale" gas promising strata of the Paleozoic in Poland and Ukraine form an entire gas-bearing complex and their potential has been until recently considered optimistic [Poprava, 2010].

Therefore, like the North American deposits [Lukin, 2010_1], during search and evaluation work within prospective areas in Volyn-Podillya attention should be paid to locations with a high content of organic matter, in which large tectonic disturbances [Krups'kyi, 2001] reveal as a result of the possible tectonic-dynamic destabilization [Solovjov, 1996, 2011] and associated with significant fracturing. It is healed by newly-formed calcite veinlet-impregnated mineralization as one of the indicators of the processes of fluid transport of substances and mechanisms of healing of fractures [Naumko, 2006]. Thus, it forms a prerequisite for the reconstruction of migrating processes, at high and even prevailing role of underlying fluid-dynamical processes in the inflow of hydrocarbon fluids from deep horizons (regardless of source), which fact has been repeatedly emphasized.

In summary, data on geochemical conditions for formation of "shale" gas [Zagnitko et al., 2011; Kurovets' et al., 2011, 2014; Hubych et al., 2012; Zagnitko, Mykhailov, 2014] in sunsurface of various regions of Ukraine (Dnipro-Donetsk basin, Bovtysk structure, Volyn-Podillya area) are considered as prospective for "shale" gas, and indicate the following.

The main types of rocks containing "shale" gas are clay and silt shales rich in organic matter. Their main minerals are: montmorillonite, kaolinite, chlorite, hydro-mica, quartz, opal, carbonates; and more rarely ore minerals and bitumen.

Component composition of gases, localized in different forms in rocks, changes within a relatively broad range, and can be very different both in the same area and at different levels of geological section and in different structures. The main components of gases are methane (up to 90 % of content) and its homologues (up to 48%), CO_2 (up to 65 %), nitrogen (up to 42 %). Also present are H_2, CO, He, H_2S. Content and distribution of components and proportions between them in different samples is rather inconsistent.

Analysis of the available data shows that the composition of these gases is similar to the composition of gases from gas fields and by-product gas from coal mines, which also fluctuate within a wide range.

During the step pyrolysis of "shale" gas, different dynamics of the degasation is manifested: and as a rule, the largest total amount of gas (up to 80 %) is exuded in the range of 400–600 °C, which is especially characteristic of methane and its homologues.

The ratio between the occluded and carbonate (in particular siderite) components of CO_2 is difficult to determine, although derivatograms clearly record intensive processes of de-carbonisation above 500 °C.

The isotopic composition of carbon in the individual components of "shale" gas varies widely: $\delta^{13}C$ from -15.7 to -32 ‰ for methane and its homologues and from -14.1 to -26,4 ‰ for CO_2 (PDB Standard). Sorbed gas (enriched with isotope ^{13}C) and gas from inclusions differ significantly in isotopic composition. Sometimes there is an irregular distribution of isotopes in individual homologues.

As the carbon isotopic composition of organic matter and carbonates in "shale" strata indicate a somewhat unusual conditions of their formation, in particular, not excluding abiogenical sources of individual components of [Zagnitko, Mykhailov, 2014]), therefore answers to genetic questions can be further to assist by isotopic and geochemical studies of carbonaceous components of "shale" gas – methane and its homologues, and carbon dioxide.

Thus, viewed together, factors and processes enumerated above that occur during the formation and transformation of gas-bearing shales, rich in organic matter, that simultaneously both originate and acummulatore "shale" gas [Hubych et al., 2012], of collectively conducide to passage of processes of gas generation and the formation of "shale" gas.

Originality

For the first time relics of renewable, almost substantially hydrocarbon anhydrous ("dry") fluids in fluid inclusions and closed pores (cavities, cracks) of shale gas promising graptolitic argillites of the Paleozoic of the Volyn-Podillya were found. This indicates the presence geo-fluid-dynamic conditions, both for the generation of hydrocarbons in the conversion of organic matter, absorbed and occluded by the mineral and organic component of rocks at the stage of katagenesis, and the inflow of deep-seated hydrocarbon fluids, and thus confirms shale gas potential of mineral resources of the region.

Practical significance

The influence of volatile compounds of closed porosity (fluid inclusions and closed pores of host rocks (graptolitic argillites)) for the total gas-bearing potential of shale-bearing strata is estimated, which will be significant, regardless of other aspects of the problem in the eventual estimate of shale gas resources (reserves).

Conclusions

1. Predominance of methane (up to 100 vol.%) in the presence of minor content of ethane, carbon dioxide and nitrogen in fluid inclusions and porous space of rocks indicates the presence of conditions for hydrocarbon component generation in processes of conversion of organic matter within studied graptolitic argillites of the Paleozoic of Volyn-Podillya.

2. Lack of steam may indicate “dryness” of hydrocarbon-bearing systems present in argillite stratum, and low values of relative gas saturation – that the transformation of organic matter as a source of volatile, especially hydrocarbon compounds happened in the presence of low (mainly, litostatic) pressures.

3. However, by one order higher relative gas saturation of veinlet calcite which healed the multitude of subvertical and horizontal cracks in argillite stratum and appearance of the stream indicates a possible inflow of deep-seated migrating paleofluids via these crack systems (powerful systems of interconnected cracks).

4. A plausible mechanism of gas generation and origin of “shale” gas is substantiated, based on the principle of unity in nature and ways of transformation of dispersed and concentrated forms of organic matter, and considering that studied graptolitic argillites and coal differ only by the amount of organic matter, are dispersed in the form of kerogen in argillites or concentrated in coal.

5. The obtained results on composition of the volatile components of fluid inclusions in minerals and closed pores of rocks supplement data on gases of hydrocarbon-holding paleosystems, their migration and localization with the formation of deposits of “shale” as the basis for establishing the nature of evoluting and migrating schemes and, therefore, peculiarities of fluid regime of processes of gas genesis within prospective deposits of the region.

6. Within “shale” gas prospective rock complexes of Paleozoic Volyn-Podillya there existed geo-fluid-dynamic conditions both for the generation of hydrocarbons in the processes of conversion of organic matter, sorbed and occluded by mineral and organic component of rocks at the stage of katagenesis and for gas arrival from deep sources as a result of the inflow of hydrocarbon fluids. Established quantitative measures of its contents are quite high, confirming gas-shale potential of subsurface of the region and call for the expansion of targeted geochemical research.

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ВУГЛЕВОДНЕВІ СПОЛУКИ ТА ВІРОГІДНИЙ МЕХАНІЗМ ГАЗОГЕНЕРАЦІЇ У ПЕРСПЕКТИВНИХ НА “СЛАНЦЕВИЙ” ГАЗ ВІДКЛАДАХ СИЛУРУ ЛЬВІВСЬКОГО ПАЛЕОЗОЙСЬКОГО ПРОГИНУ

Мета. Дослідження складу газу закритої пористості (флюїдні включення у мінералах і закриті пори порід) перспективно газоносних граполітових аргілітів силуру Львівського палеозойського прогину та обґрунтування вірогідного механізму і динаміки газогенерації під час формування “сланцевого” газу у продуктивних верствах чорносланцевих формацій регіону. **Методика.** Склад летких сполук флюїдних включень у мінералах і закритих пор порід, їхні відносні газонасиченість і водонасиченість визначали мас-спектрометричним хімічним методом. Включення і закриті пори розкривали за допомогою розчавлювання стандартної проби (наважка 200 мг, фракція +1–2 мм) у невеликій металевій циліндричній ступці між двома плоскопаралельними твердосплавними (побєдітовими) поверхнями в умовах високого вакууму (порядка $1 \cdot 10^{-3}$ Па). **Результати.** За даними мінералофлюїдологічних досліджень у газовій фазі флюїдних включень у мінералах і закритих пор граптолітових аргілітів силуру Львівського палеозойського прогину домінує метан (до 100 об. %) за незначних вмістів етану, діоксиду вуглецю, азоту. Відсутність пари води може свідчити про “сухість” вуглеводневмісних систем, а низькі значення відносної газонасиченості – про перетворення органічної речовини як джерела летких вуглеводневих сполук за невисоких (головно, літостатичних) тисків. Це свідчить про реальність перебігу процесів газоутворення під час трансформації органічної речовини аргілітових верств. На порядок вища відносна газонасиченість включень у кальциті, яким заліковані субвертикальні тріщини в аргілітах, і поява пари води вказує на ймовірний приплив глибинних мігрувальних флюїдів потужними тріщинними системами. Обґрунтовано вірогідний механізм і динаміку газогенерації з подальшим захопленням газу у вільному стані та сорбцією і окклюзією породами, інтенсифікований впливом глибинних флюїдів. Він основується на зіставленні даних про склад летких сполук флюїдних включень у мінералах і закритих пор перспективно газоносних аргілітів та сорбційно-генераційні процеси утворення метану у вугіллі, виходячи з принципової єдності природи перетворення розсіяної і концентрованої форм органічної речовини. **Наукова новизна.** Вперше у флюїдних включеннях у мінералах і закритих порах (кавернах, тріщинах) перспективних на “сланцевий” газ граптолітових аргілітів палеозою Волино-Поділля встановлено релікти відновних, практично істотно водневодневих безводних (“сухих”) флюїдів. Це вказує на наявність геофлюїдодинамічних умов, як для генерації вуглеводнів у процесах перетворення органічної речовини, сорбованих і окклюдованих мінеральною і органічною складовою порід на стадії катагенезу, так і припливу глибинних вуглеводневих флюїдів, і, отже, підтверджує газосланцевий потенціал надр регіону. **Практична значущість.** Оцінено вплив летких сполук закритої пористості (флюїдні включення у мінералах і закриті пори вмісних порід (граптолітових аргілітів) на сумарну потенційну газоносність сланцевовмісних верств, що матиме значення (не заторкуючи інших аспектів проблеми) за можливого підрахунку ресурсів (запасів) “сланцевого” газу.

Ключові слова: леткі компоненти; флюїдні включення; закриті пори; “сланцевий” газ; граптолітові аргіліти; силур; Львівський палеозойський прогин.

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УГЛЕВОДОРОДНЫЕ СОЕДИНЕНИЯ И ВЕРОЯТНЫЙ МЕХАНИЗМ ГАЗОГЕНЕРАЦИИ В ПЕРСПЕКТИВНЫХ НА "СЛАНЦЕВЫЙ" ГАЗ ОТЛОЖЕНИЯХ СИЛУРА ЛЬВОВСКОГО ПАЛЕОЗОЙСКОГО ПРОГИБА

Цель. Исследование состава газа закрытой пористости (флюидные включения в минералах и закрытые поры пород) перспективно газоносных граполитовых аргиллитов силура Львовского палеозойского прогиба и обоснование вероятного механизма и динамики газогенерации при формировании "сланцевого" газа в продуктивных толщах черносланцевых формаций региона. **Методика.** Состав летучих соединений флюидных включений в минералах и закрытых пор пород, их относительные газонасыщенность и водонасыщенность определяли масс-спектрометрическим химическим методом. Включения и закрытые поры раскрывали путем раздавливания стандартной пробы (навеска 200 мг, фракция +1-2 мм) в небольшой металлической цилиндрической ступке между двумя плоскопараллельными твердосплавными (победитовыми) поверхностями в условиях высокого вакуума (порядка $1 \cdot 10^{-3}$ Па). **Результаты.** По данным минералофлюидологических исследований в газовой фазе флюидных включений в минералах и закрытых пор граполитовых аргиллитов силура Львовского палеозойского прогиба доминирует метан (до 100 об. %) при незначительных содержаниях этана, диоксида углерода, азота. Отсутствие паров воды может свидетельствовать о "сухости" углеводородосодержащих систем, а низкие значения относительной газонасыщенности – о превращении органического вещества в качестве источника летучих углеводородных соединений при невысоких (приимущественно, литостатических) давлениях. Это свидетельствует о реальности прохождения процессов газообразования при трансформации органического вещества аргиллитовых толщ. На порядок высшая относительная газонасыщенность включений в кальците, которым залечены субвертикальные трещины в аргиллитах, и появление паров воды указывает на вероятный приток глубинных мигрирующих флюидов мощными трещинными системами. Обоснован вероятный механизм и динамика газогенерации с дальнейшим захватом газа в свободном состоянии и сорбцией и окклюзией породами, интенсифицированный влиянием глубинных флюидов. Он базируется на сопоставлении данных о составе летучих соединений флюидных включений в минералах и закрытых пор перспективно газоносных аргиллитов и сорбционно-генерационных процессах образования метана в углях, исходя из принципиального единства природы преобразования рассеянной и концентрированной форм органического вещества. **Научная новизна.** Впервые во флюидных включениях в минералах и закрытых порах (кавернах, трещинах) перспективных на "сланцевий" газ граптолитовых аргиллитов палеозоя Волино-Подолии выявлены реликты восстановленных, практически существенно углеводородных безводных ("сухих") флюидов. Это указывает на наличие геофлюидодинамических условий, как для генерации углеводородов в процессах превращения органического вещества, сорбированных и окклюдированных минеральной и органической составляющими пород на стадии катагенеза, так и притока глубинных углеводородных флюидов, и, таким образом, подтверждает газосланцевый потенциал недр региона. **Практическое значение.** Оценено влияние летучих соединений закрытой пористости (флюидные включения в минералах и закрытые поры вмещающих пород (граптолитовых аргиллитов) на суммарную потенциальную газоносность сланцевовмещающих толщ, что будет иметь значение (не затрагивая других аспектов проблемы) при возможном подсчете ресурсов (запасов) "сланцевого" газа.

Ключевые слова: летучие компоненты; флюидные включения; закрытые поры; "сланцевый" газ; граптолитовые аргиллиты; силур; Львовский палеозойский прогиб.

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