PORE SPACE CHANGE OF VARIOUS LITHOTYPES OF THE KEROGEN DOMANIC ROCKS AT DIFFERENT HEATING RATES

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Abstract. The results of pore space changes as a result of heating Domanik Formation rock samples at different heating rates are shown. Microtomography method revealed that after heating in significant changes may arise, lens-like large pores can be formed, the number of pores and their coherence increase. It was found that changes in the pore space depend on the texture of rocks, the amount of organic matter and its degree of maturity, with all the factors must be considered together. Heating rate also influences the change in the pore space. The results should been considered in the retrieving of the natural reservoirs formation.

Keywords: Domanik Formation, pore space, samples heating, kerogen cracking
DOI: https://doi.org/10.18599/grs.19.3.17

For citation: Gafurova D.R., Korost D.V., Kozlova E.V., Kalmykov A.G., Kalmykov G.A. Pore Space Change of Various Lithotypes of the Kerogen Domanic Rocks at Different Heating Rates. *Georesursy = Georesources.* 2017. V. 19. No. 3. Part 2. Pp. 255-263. DOI: https://doi.org/10.18599/grs.19.3.17

Introduction

Currently, researchers and oil companies are paying special attention to unconventional oil and gas reservoirs, such as Bazhenov and Domanic formations. This is due to a decrease in the amount of conventional oil reserves and an increase in the share of reserves belonging to high-carbon formations. At the same time, unlike conventional reservoirs, the regularities of field distribution are not known at present for unconventional reservoirs; many wells drilled are yet dry. Therefore, the researchers are faced with the task of finding these regularities and predicting the most productive areas.

One way to understand the structure and distribution of intervals with high porosity is to develop a theory of pores generation in high-carbon formations. The works carried out abroad are usually devoted to identifying the patterns of kerogen conversion under natural conditions for the formation of oil and gas fields (Ishiwatary et al., 1979; Burnham et al., 1984; Behar et al., 1992). However, these studies consider first of all the mechanism and kinetics of hydrocarbons formation and do not consider changes occurring in the pore space due to the transformation of organic matter (OM).

Temperature, time and pressure are the main factors influencing the transformation of organic matter of the oil-parent rock, leading to the formation of new pores and changes in permeability (Bazhenova, 2000). At present, a number of experiments are being carried out, mainly to simulate the thermal impact on rocks and to investigate the transformation of voids (Jing Zhao et al., 2012; Kobchenko et al., 2011; Tisot, 1967; Korost et al., 2012; Tiwari et al., 2013, etc.). However, these works are not generalized by a single technology, they do not consider the influence of the heating rate on the simulation, and, first of all, do not consider the Domanic Formation as an object that has a structure different from other objects under study and which provokes increased interest among Russian geologists and representatives of oil companies.

In this paper, we consider the change in the internal structure of rocks, in particular, the void space, as a result of laboratory modeling of generation and primary migration of hydrocarbons. Earlier, the authors of the article carried out a number of similar experiments in which the degree of change in the pore space of samples was studied depending on the texture features of rocks and the degree of their saturation with organic matter (Gilyazetdinova, 2016).

The experiment described is based on the experience of foreign and Russian scientists (Table 1). The heating rates in these cases were selected in an average way: based on sample sizes, heating temperatures and instrumentation capabilities and programs. At the same time, the heating rate of rocks and their composition and texture, in our opinion, can play a significant role in the degree of change in the internal structure of rocks. This determined the main task of this work: the characterization and analysis of the degree of change in the rocks as a result of various heating modes of samples and setting the influence of the heating rate on the transformation of void space in various samples.

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Experiment	Formation	Corg, %	Size, cm	Temperature, °C	Heating method	Newly formed elements of pore space
Institute of Mining Technology, Taiyuan University of Technology (China), Jing zhao et al., 2012	Daqing	15,02	0,5x1	100, 200, 300, 400, 500, 600	At all temperatures were held for 30 min	Fractures, pores
	Yan'an	7,85	0,5x1			
Department of Chemical Engineering, University of Utah, Salt Lake City (United States), P. Tiwari et al., 2013	Green river	20,27	2,54x5,08	350, 425, 500	100ºC/min were heated to the estimeated temperature and were held for 24 hours	Fractures, pores
		10,33	2,54x5,08			
		0,1546	2,54x5,08			
Laramie Petroleum Research Center, Bureau of Mines, Department of the Interior, Laramie, Wyo. (United States) P. R. TISOT, 1967	Green river	0,006	1,9/3,175	510, 815	5ºC/hour to 399ºC and were held 12 hours, then heating до 510ºC and were held 2 hours	Fractures
		3,9	1,9/3,175			
		8,1	1,9/3,175			
		15	1,9/3,175			
		18	1,9/3,175			
		35,1	1,9/3,175			
Geological Faculty of Lomonosov Moscow State University, Petroleum Geology Department (Russia), D.V.Korost, 2011	Domanic	13,08	0,3	300, 400, 470, 510	10ºC/min then were held 5 min, at temp. 470, 510 2ºC/min и 5 min were held	Fractures
Physics of Geological Processes, University of Oslo, Oslo, (Norway), Maya Kobchenko et al., 2011	Green river	9,92	0,5x0,5	400	1ºC/min	Fractures

Table 1. Comparison of the rock heating modes in the experiments of Russian and foreign scientists

Methods for the study of rocks

To study the structure and composition of the rocks selected for the experiment, a complex of studies was carried out, including: X-ray diffractometry on the Rigaku Ultima-IV unit (Japan), study of thin sections on the Leica DM EP optical laboratory microscope, microprobe based on a scanning electron Microscope (SEM) “Jeol JSM-6480L” with a combined system of X-ray spectral microanalysis. Scanning electronic images are obtained in secondary electrons (surface morphology)

The next stage of the investigation consisted in scanning of cylindrical samples with a diameter of 3 mm on a computer X-ray microtomograph (microCT) SkyScan-1172. The survey was carried out with a spatial resolution of about 1.5 μm, on an Al 0.5 mm filter at a source voltage of 70 kV and a current strength of 129 μA. On the resulting x-ray sections of the sample, a darker color corresponded to a smaller X-ray density of the medium, and a lighter color – to a larger density (Stock, 2009).

The geochemical characteristics of organic matter were obtained on a Rock-Eval-6 pyrolyzator (Espitalie, 1984; Tissot and Welte, 1981; Lopatin and Emets, 1987).

Collection of samples

For the experiment, a collection of rock samples was selected from the kerogen-saturated Domanic formation of the Volga-Ural oil and gas basin with various parameters including the content of organic matter, the degree of maturity, and texture characteristics (Gilyazetdinova, 2015). Among the Domanic rocks, with a high content of kerogen and bitumen, the siliceous-carbonate rocks of the South Tatar arch (Semilukskian and Mendinskian horizons, the Franskian stage of the Upper Devonian) were chosen because of the low content of pyrite in them, which distorts the X-ray density sections (as, for example, in the rocks of the Bazhenov Formation of the Western Siberian oil and gas basin).

Samples are characterized by different contents of organic matter (from 5.66% to 30.23%), different textures and mineral composition. The rock composition is predominantly siliceous-carbonate. The composition of the samples differs, primarily, by the content of the siliceous component (Table 2).

Sample 1 is characterized by a layered texture, which is recorded due to the presence of carbonate detritus

No	Rock	Mineral composition, Main/ Silic./Carb., %	Texture	TOC, %	Degree of transformation
1	Kerogen-siliceous-carbonate	4/20/37	Laminated	30	PK3
2	Carbonate rock with kerogen	4/0/89	Laminated	6	MK2
3	Kerogen-siliceous-carbonate	2/17/64	Massive	13	PK3

Table 2. General lithological and geochemical characteristics of the samples

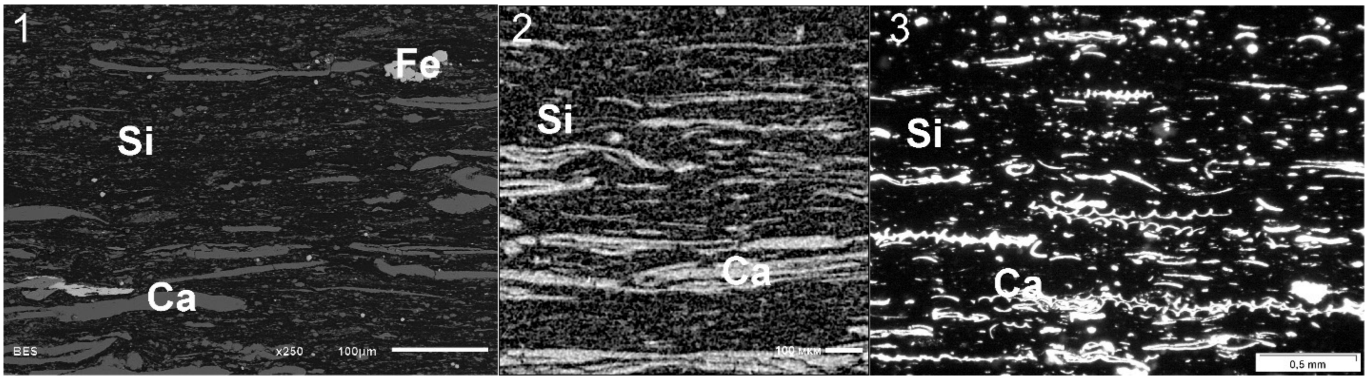

Fig. 1. Sample 1: 1 – SEM photograph, 2 – microCT cut, 3 – photograph of the section in crossed Nicol prisms

(Fig. 1). Matrix consists of a siliceous material, which is well distinguished on x-ray density microtech slices and has a weakly expressed intrinsic layered microtexture. The content of organic carbon in the sample reaches 30%.

Sample 2 is characterized by minimal values of organic carbon content (6%) among the selected samples. The rock contains organic interlayers in the carbonate matrix. The bulk of the rock is represented by a massive carbonate material, against which thin (up to 30 µm) interlayers saturated with organic matter are noted (Fig. 2).

Sample 3 has a massive texture. Bioclasts cemented with siliceous substance are distinguished in the rock composition (Fig. 3), while in the rock it is possible to assume the presence of stratification. The content of organic carbon in the rock is 13%.

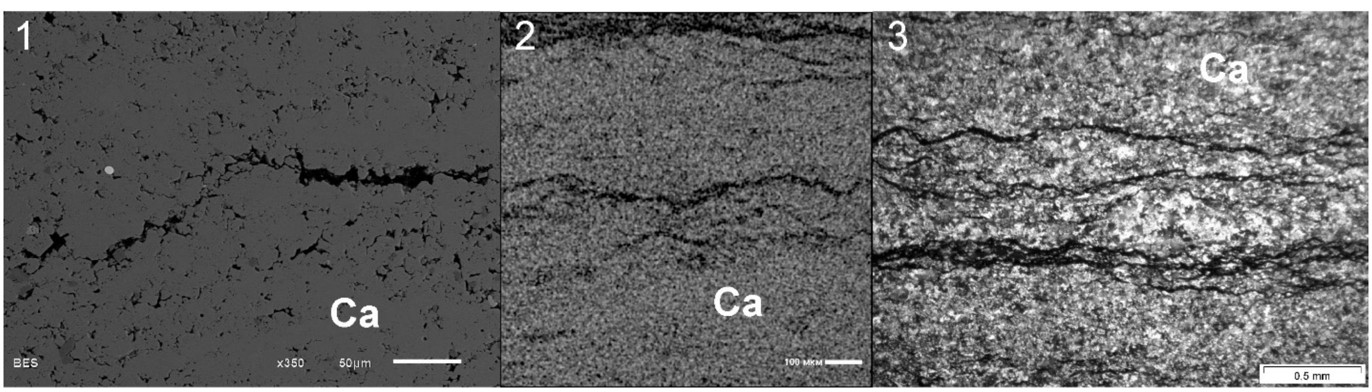

Fig. 2. Sample 2: 1 – SEM photograph, 2 – microCT cut, 3 – photograph of the section in crossed Nicol prisms

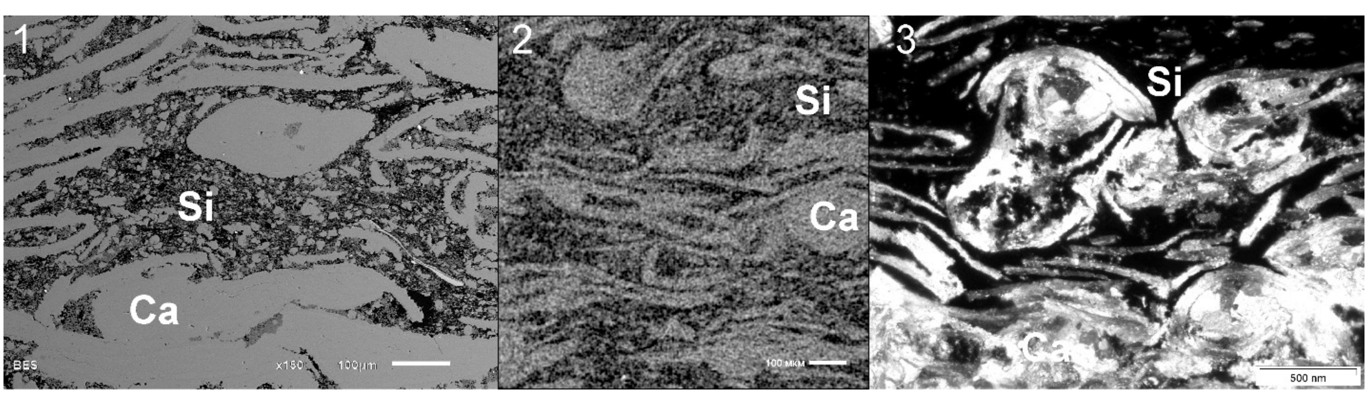

Fig. 3. Sample 3: 1 – SEM photograph, 2 – microCT cut, 3 – photograph of the section in crossed Nicol prisms

Methods of the experiment

The laboratory experiment consisted in simulating the formation of pore space by generating a shock wave in an undisturbed rock sample (a microcylinder with a diameter of about 3 mm and a height of 3-5 mm) by heating in a nitrogen atmosphere according to a given temperature program and observing changes in the pore space structure. The experiments were based on changes occurring in three duplicating cylinders of one sample placed in a RockEval 6 pyrolyzer and heated with different heating rates. At a temperature of 300 °C, the samples were held for 5 minutes, while the peak S1, characterizing the content of light hydrocarbons, was recorded. Then, heating occurred at rates of 2, 10 and 30 °C/min from 300 °C to 500 °C. The temperature of 500 °C was chosen on the basis of preliminary experiments on powders for which the parameter S2 (hydrocarbons release in the temperature range 300-650 °C) was determined and the temperature of the release peak was chosen.

To monitor changes in the construction, rock structure and pore space, a computer microtomograph was used. The color of the phase, obtained on X-ray density sections of the sample, characterizes X-ray absorption. X-ray absorption depends on the density of mineral and non-mineral components of rocks. X-ray absorption will be minimal for organic matter due to the low density of kerogen component in the rock. Taking into account the fact that in the studied rocks, empty space as such is practically absent (the OM is filled), the entire volume corresponding to the intermineral phase of the rock, that is, the void space with the minimum X-ray absorption is taken as OM.

Based on the data of the microCT, the content of OM in unchanged samples, as well as the content of OM and newly formed pores in heated samples was measured for all samples, with all other conditions being equal. The evaluation of OM/porosity was carried out using computer analysis: the separation of X-ray contrast phases on the basis of the brightnesses characteristic for them (grayscale). The volume calculation of the phase was carried out for the selected brightness corresponding to the pore space of rocks. To estimate the transformation of the void space in the sample, in particular, the calculated volumes of pore connectivity were estimated. The “connectivity” parameter characterizes the degree of connection of the emitted elements in a void space in the volume of the sample. This analysis allows us to calculate the number and size of each individual object (pores). Based on the statistical analysis, the volume fraction of the largest cluster is estimated, which characterizes the element connectivity (in this case, voids) in the rock volume (Fig. 4). The parameter “connectivity” allows estimating the degree of change in the void space, since during the rock heating, the pores, lenses and interlayers are modified and are often combined into a single system.

Results of the research

As a result of heating at different rates, there were significant changes in the matrix of the rock in sample 1. Lenticular voids appeared with the opening up to 0.3-0.4 mm (Fig. 5). At the same time, the heating rate does not affect the weight loss of the samples; the weight change was constant and amounted to about 27%. Also objects connectivity was constant, regardless of the heating rate, and was 99%. However, the different heating rates had a significant effect on the change in porosity, the number of objects in the sample, and the lenses openness. The calculated values of porosity have changed depending on the heating rate of 2 °C /min, 10 °C/min and 30 °C/min for 23, 54 and 61%, respectively. At the same time, visually the maximum capacity of the newly formed voids falls on a sample heated at a rate of 2 °C/min and equal to 0.4 mm (Fig. 5). In this sample, the largest (threefold) change was also observed in the number of void space elements – micro-voids, which were formed as a result of the OM transformation. The results of the change in characteristics as an influence of heating are given in Table 3.

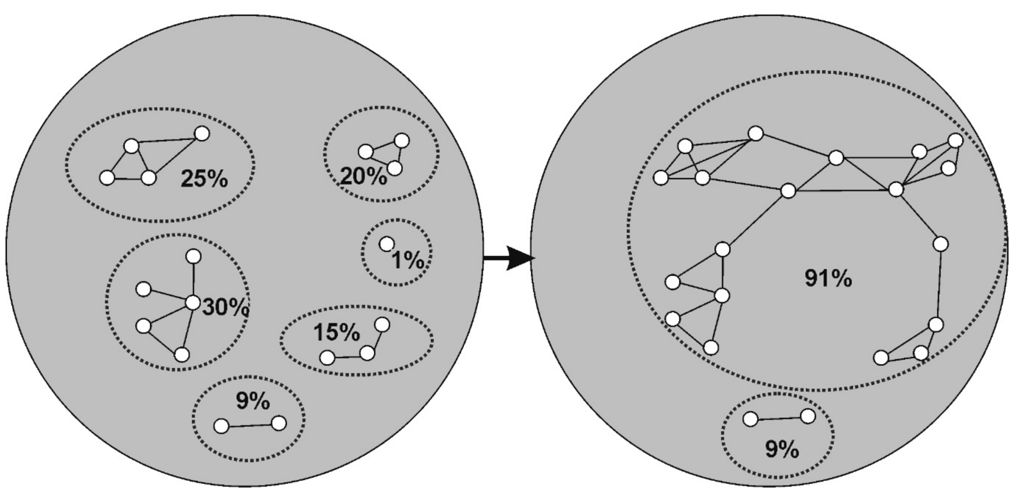

Fig. 4. Scheme of changes in the void space connectivity as a result of the sample heating

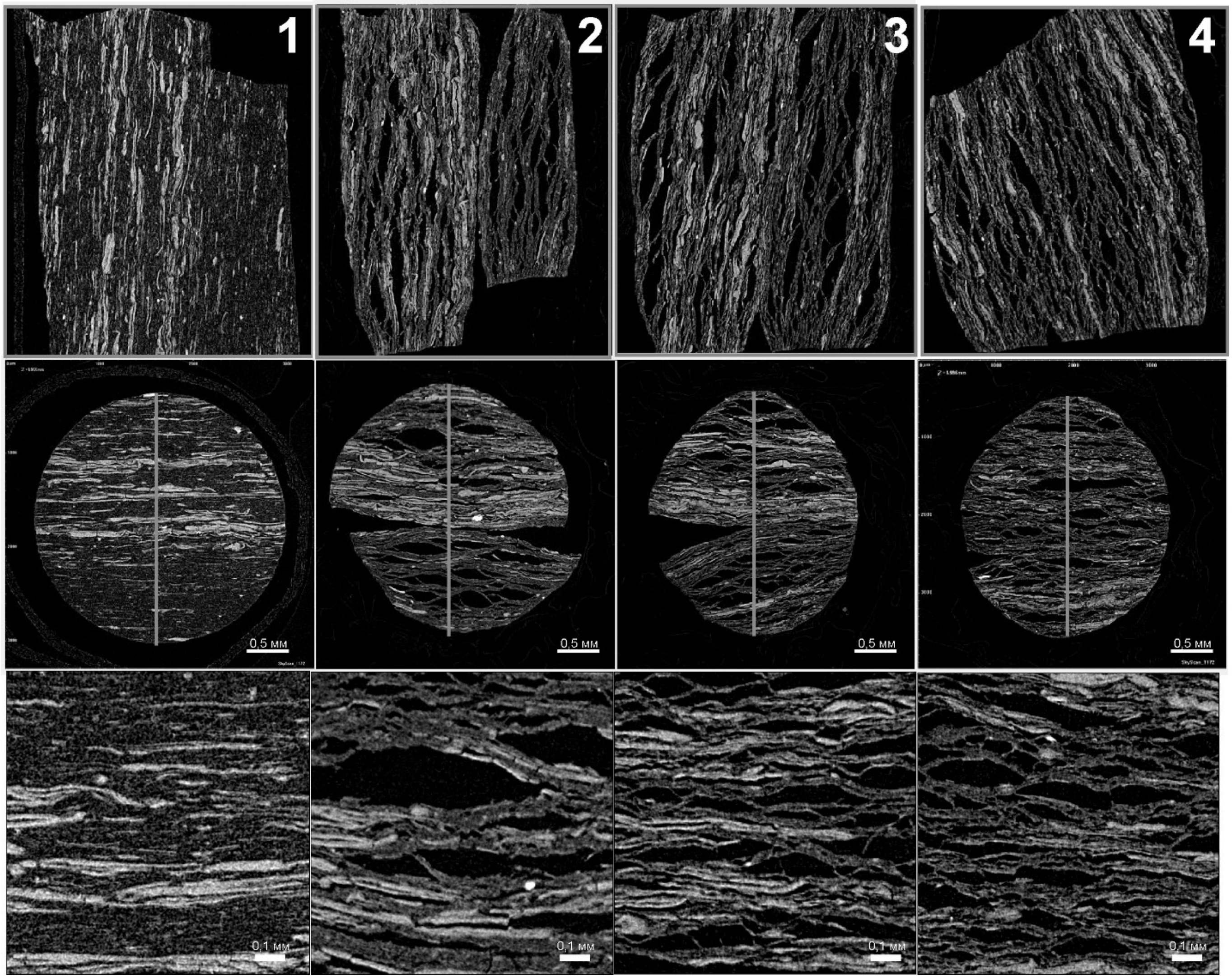

Fig. 5. X-ray density sections of sample 1 (cube edge 1 mm): 1 – unchanged sample, 2 – 2 °C/min, 3 – 10 °C/min, 4 – 30 °C/min

Heating rate	TOC, %	S1, mgHc/g	S2, mgHc/g	Porosity variation, %	Coherence, %	Number of objects (pores)	Weight variation (loss), %
raw	30	10,26	198,64	23,4	99,1	5930	26,69
2°C/min		5,32	102,5		96,48	16408	
raw	30	10,26	198,64	54,49	98,9	7050	27,81
10°C/min		5,11	120		99,1	8151	
raw	30	10,26	198,64	60,51	99,3	6023	28,57
30°C/min		3,93	97,86		99,48	9886	

Table 3. Results of sample 1heating

In the structure of sample 2, characterized by a minimum content of organic matter, the smallest changes occurred (Fig. 6). The pore connectivity remained the same and amounted to 30-35%, weight loss for all samples was about 4%, and the number of objects in the void space increased by about 20% (Table 4). It is worth noting that, just like in the first sample, the trend of variation in the calculated values of the porosity, depending on the rate of heating, was similar and amounted to 27, 55 and 55%.

In sample 3 with a massive texture, a different character of the changes was observed. In this sample, there was no significant expansion of interlayers filled with organic matter, but the void space was transformed due to the formation of new pores and channels connecting the original elements of the void space of the rock (Fig. 7). The pores connectivity in the samples increased to 85-95%, and the change in porosity with the same weight loss was 117%, 99% and 76% (Table 5). In this case, the number of free-standing elements of the void space decreased by at least 2 times.

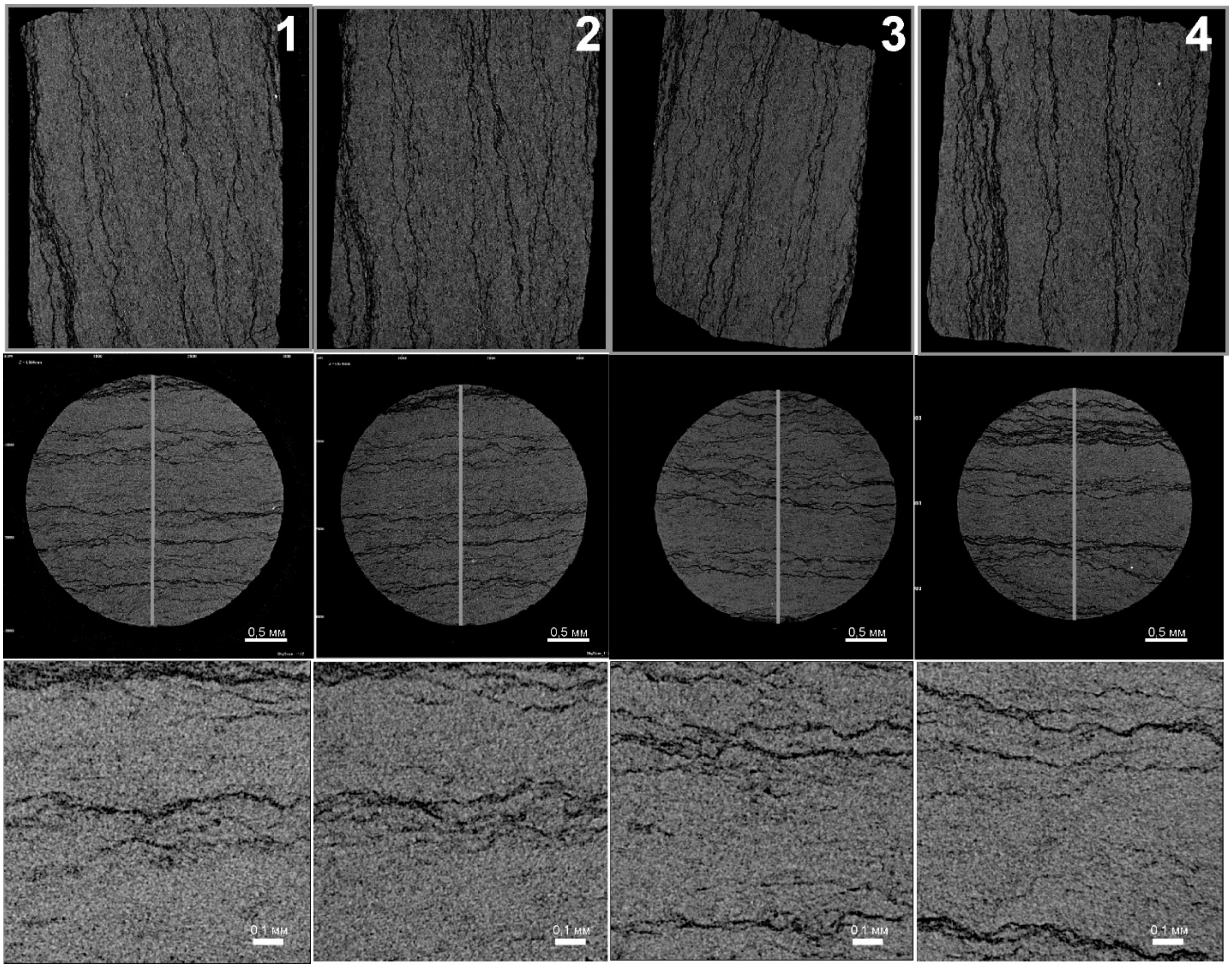

Fig. 6. X-ray density sections of sample 2 (cube edge 1 mm): 1 – unchanged sample, 2 – 2 °C/min, 3 – 10 °C/min, 4 – 30 °C/min

Heating rate	TOC, %	S1, mgHc/g	S2, mgHc/g	Porosity variation, %	Coherence, %	Number of objects (pores)	Weight variation (loss), %
raw	6	2,48	32,78	27,35	32,06	20542	3,85
2°C/min		1,44	17,29		32,32	25832	
raw	6	2,48	32,78	54,55	30,65	23502	3,04
10°C/ min		1,56	18,53		35,2	25614	
raw	6	2,48	32,78	54,71	39,6	19138	4,82
30°C/ min		1,51	19,32		39,27	23038	

Table 4. Results of sample 2 heating

The discussion of the results

As a result of the conducted experiments, a significant change in the pore space was observed, depending on the amount of organic matter. Probably, the formation of large lenses in sample 1 (Fig. 5) is associated with an increase in pore pressure in interlayers saturated with organic matter in the process of new hydrocarbons generation. Considering the organic matter content in the rock and its low maturity, the formation of new hydrocarbons leads to an anomalously high pore pressure, and, as a consequence, to rupture of interlayers, the formation of large lenticular voids.

Another pattern is observed in sample 2, the original thin interlayers, saturated with organic matter, retained their shape, no visible large deformations in the rock occurred. The low content of organic matter and its partial transformation do not lead to the formation of large visible voids. Probably, newly formed hydrocarbons migrate in a small volume in already existing interlayers, thereby releasing voids previously filled with bitumen. The volume of newly formed hydrocarbons is so small that it is not enough to cause high pore pressure in the pores and lead to the rupture of bonds. It is worth noting that in the second

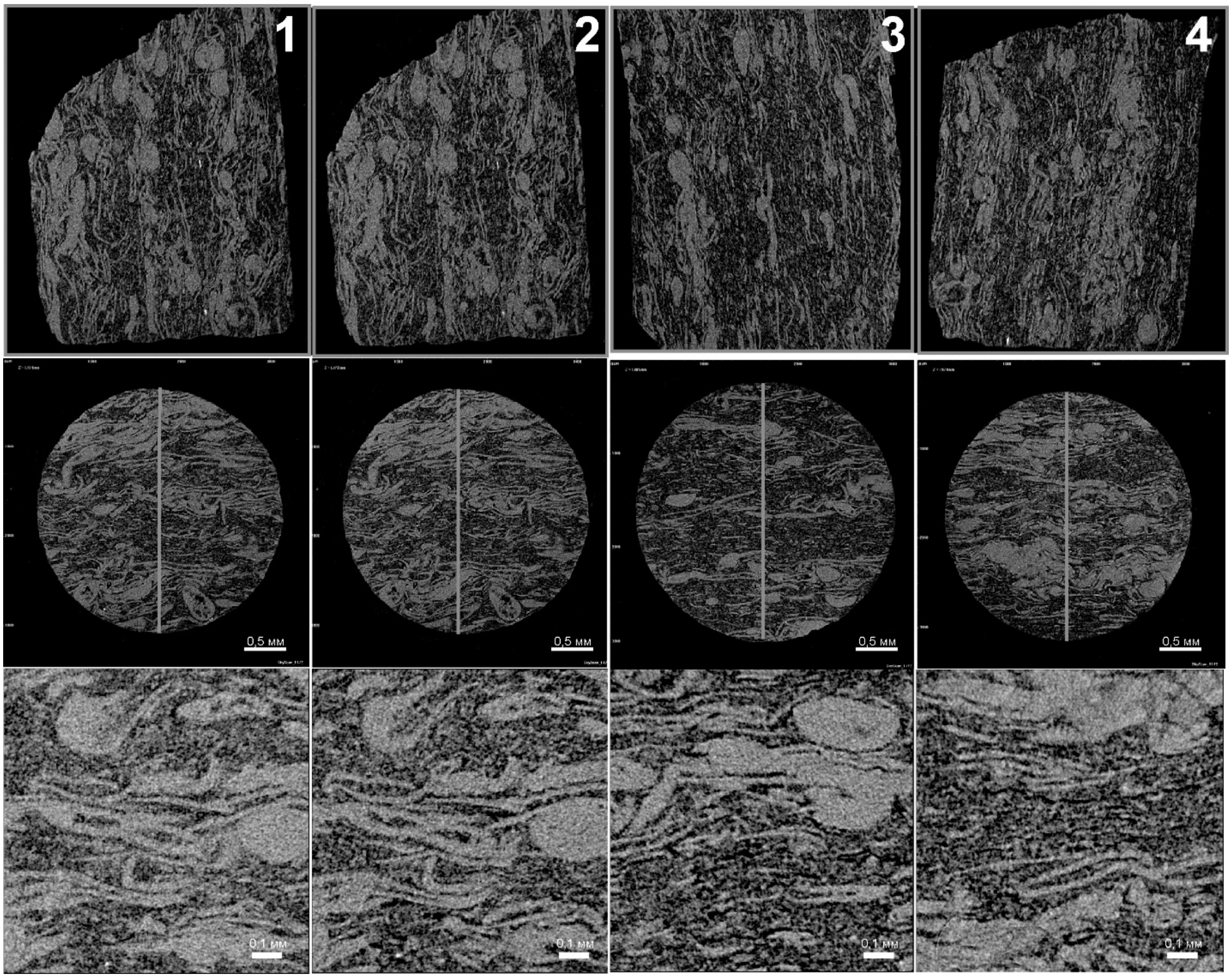

Fig. 7. X-ray density sections of sample 3 (cube edge 1 mm): 1 – unchanged sample, 2 – 2 °C/min, 3 – 10 °C/min, 4 – 30 °C/min

Heating rate	TOC, %	S1, mgHc/g	S2, mgHc/g	Porosity variation, %	Coherence, %	Number of objects (pores)	Weight variation (loss), %
raw	13	5,35	82,81	116,72	18,68	35439	9,62
2°C/ min		1,77	28,18		84,85	16767	
raw	13	5,35	82,81	98,83	75,69	75997	9,58
10°C/ min		2,91	45,63		94,52	37177	
raw	13	5,35	82,81	76,22	37,42	85844	8,45
30°C/ min		2,16	37,29		84,46	17130	

Table 5. Results of sample 3 heating

sample the organic matter had a greater maturity, a smaller generation potential (parameter S2 is much lower), which can determine a smaller volume of formed pore space. Thus, it can be concluded that the amount of organic matter and its stage of catagenesis influence the transformation of voids simultaneously (Gilyazetdinova, 2015).

As was shown above, the pattern of porosity variation for samples 1 and 2 is the same and has the appearance of an increasing function that emerges on the plateau, while for sample 3 a smooth decrease in porosity variation with increasing heating rate is observed (Fig. 8). The observed regularities are not associated with the maturity stage, since samples 1 and 2 are at different stages of catagenesis, and also do not directly depend on the composition of the samples, since in sample 3 the average content of carbonates, organic matter and silica is compared with the other two. Most probably this difference is explained by the morphology of sample 3, possibly carbonate bioclasts prevent expansion of pores, and therefore the reservoir pressure cannot create lenses.

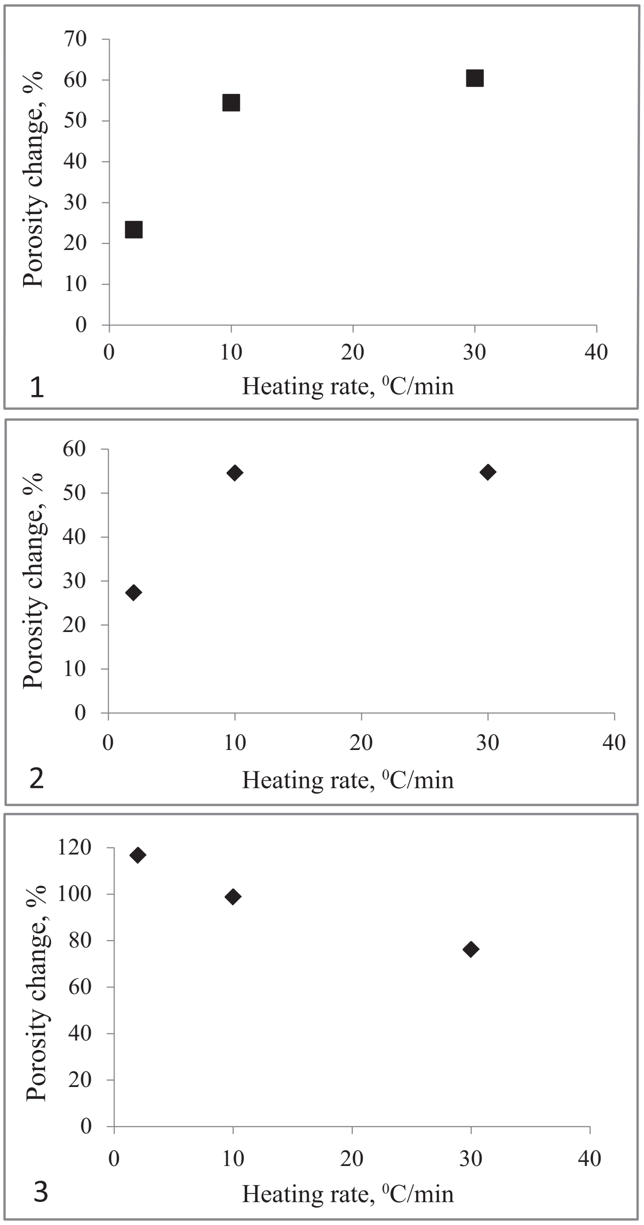

Fig. 8. Graphs of ΔKpCT dependence (porosity change) on the rock heating rate: 1 – sample 1; 2 – sample 2; 3 – sample 3

Another option is the possible inhibitory capacity of such bioclasts. Nevertheless, according to the results of the studies, the following conclusion can be drawn: the texture of the rock is an important factor affecting the formation of porous structure and, probably, influencing the degree of organic matter transformation (Gilyazetdinova, 2015).

Thus, on the basis of the work done, the following conclusions can be drawn:

1. The heating rates play a rather large role in the degree of the porous space transformation. However, these changes in different types of rocks take place in different ways. It is necessary to carry out additional experiments on rocks with different composition and texture in order to reveal direct dependences of the influence of various components and their mutual arrangement on the formation process of a porous structure. Nevertheless, the results obtained are important in modeling the process, it is necessary to take into account these factors when modeling the formation of reservoirs in Domanic deposits.

2. The degree of catagenetic transformation must also be taken into account in modeling. However, there was no direct effect on the change in pore space. At the same time, it is obvious that under the same conditions, more hydrocarbons are formed from less mature organic matter, which will lead to the formation of a larger space. Further studies should also take into account this factor.

3. The correctly selected heating mode and experimental conditions make it possible to simulate a long process of the pore space generation in the Domanic Formation in the framework of a laboratory experiment. The result obtained may prove to be the key in the search for new deposits and regulations of natural reservoirs distribution.

Acknowledgements

The work was supported by the Russian Foundation for Basic Research, grant No. 16-35-00576.

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Manuscript received 28 July 2017;
Accepted 05 September 2017; Published 15 October 2017