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## Laboratory studies of the behavior of organic matter of the Bazhenov deposits during thermal effects

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**Abstract.** Currently, the role of unconventional facilities for hydrocarbons is increasing. Such objects include the Domanik rocks (Republic of Tatarstan) and Bazhenov deposits (Western Siberia). The article presents the results of studying the type of organic matter of the Bazhenov suite and studying the process of pyrolysis of organic matter. It is established that the formation of new free hydrocarbon radicals occurs at temperatures up to 350°C (pyrolysis of organic matter). This indicates that the rocks of the Bazhenov suite did not fully realize their hydrocarbon potential. The deposits of the “normal” section of the Bazhenov suite not only contain a large amount of ready and hard to recover hydrocarbons, but also have an additional generation potential.

### Introduction and Methodology

Currently, there is a decrease in the production of traditional oil in Russia. There is a need to identify, study and introduce into the development of hydrocarbons unconventional reservoirs. Bitumen deposits, carbonate reservoirs, etc. are among such objects. Among the promising for the search and extraction of hydrocarbons are deposits of "shale" formations. On the territory of the Republic of Tatarstan, a number of such objects are Domanik rocks [1, 2, 3], and in Western Siberia the Bazhenov suite is the most famous and promising shale formation [4]. The formation of the Bazhenov suite took place during the Volga and early Berriane centuries in the relatively deep-water epicontinental West Siberian Sea.

The object of research of this work is the rocks of the Bazhenov suite and the Achimov formation. To perform the work, a complex of studies was used: traditional macro-structural-texture analysis, optical methods (Leica microscope), X-ray phase analysis (diffractometer

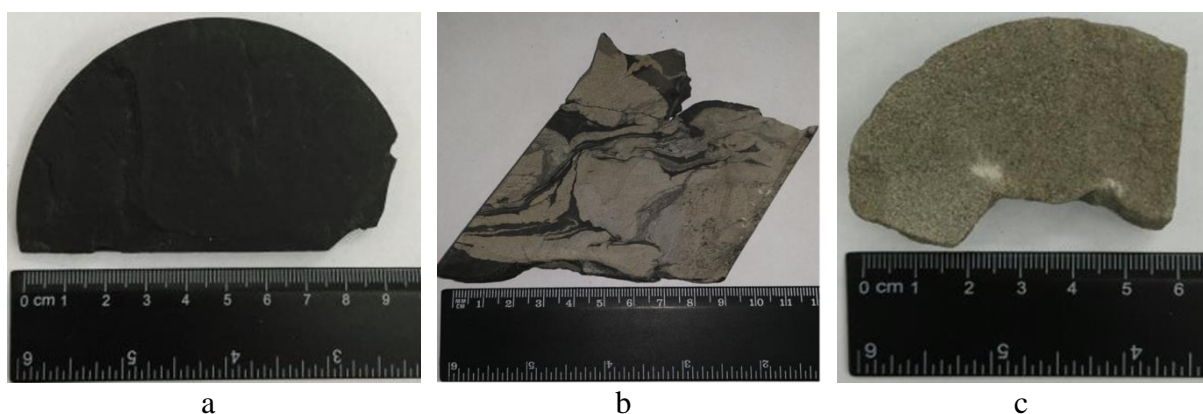


DRON-3M), electron paramagnetic analysis (spectrometer CMS8400 3cm range), scanning electron microscopy (Philips XL-30).

## Results and Discussions

Within the study area, two types of sections of the Bazhenov suite are distinguished: “normal” and “anomalous”. Rocks of the “normal” section are composed of homogeneous black, dense, and platy argillites, and the “anomalous” section differs sharply in structural and textural characteristics. Typical minerals of rocks of the Bazhenov suite are fine-grained quartz, plagioclase (albite), biotite, muscovite, chlorite. The rocks also include clay minerals: illite, kaolinite, and sites of ore mineral extraction.

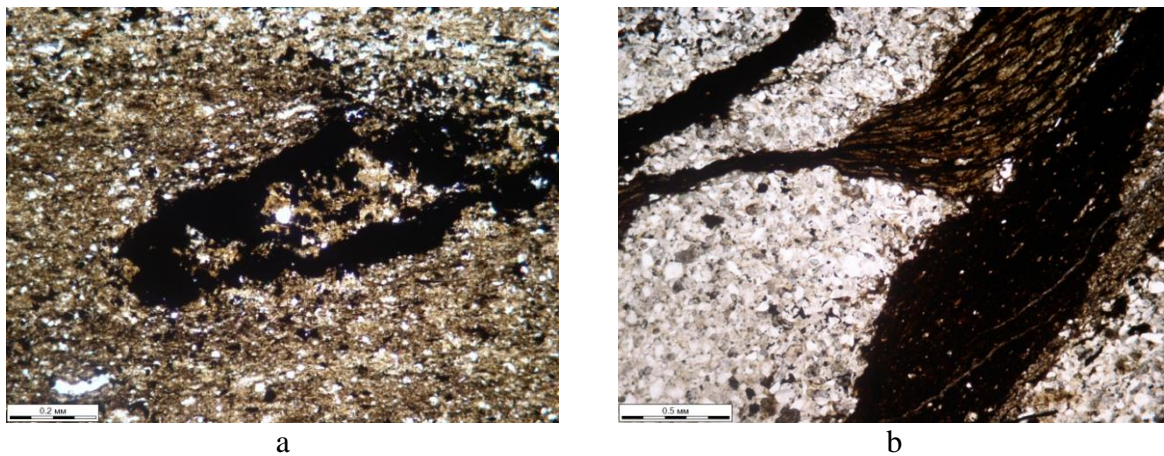
In the rocks of the “anomalous” section, on the background of homogeneous gray, fine-grained sandstones, interlayers of black, strongly deformed, dense argillites stand out. The Achimov formation is more homogeneous and is composed of gray, fine-grained, quartz-feldspathic sandstones. At present, the main mining operations are carried out from sections of rocks corresponding to the “anomalous” type of Bazhenov deposits (Figure 1).



**Figure 1.** Structural and textural features of the studied rocks: a) the rocks of the “normal” section of the Bazhenov suite; b) typical rocks of “anomalous” section; c) rocks of the Achimov suite.

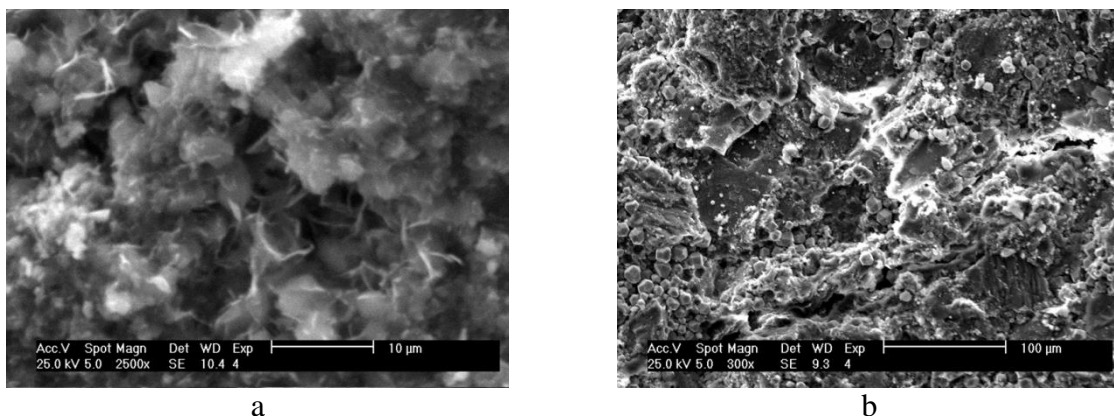
In the process of research, special attention was paid to the study of the type of organic matter, the characteristics of its distribution and behavior during thermal methods of exposure to the rock (Figure 2a, b).

The rocks the “normal” section of the Bazhenov suite are characterized by heterogeneity of distribution and difference in the shape and size of organic matter secretions: from diffuse, disseminated forms to contents in the form of large clusters, lenticular secretions with residual fragments of detritus. Fragments of detritus are replaced by ore minerals with preservation of the structure (Figure 2a).



**Figure 2.** Features of the distribution of organic matter in the Bazhenov suite: a) spotted accumulations of organic matter, the rocks of the “normal” section of the Bazhenov suite; b) typical rocks of "anomalous" section of the Bazhenov suite.

According to the results of scanning electron microscopy with microprobe analysis, it was found that the rocks of the Bazhenov suite within the studied wells have microporosity. Pores in different parts of the rock differ in size and shape. In samples of wells from deeper depth an interval, the presence of “felt” forms of illite is noted, which fulfills the void space, but the pores remain permeable. The presence of grains of the secondary quartz is noted in larger pores. In the rocks of the “normal” section of the Bazhenov suite in association with clay minerals in the void space, there are excretions of fine pyrite, the larger precipitates – framboids scattered throughout the rock.

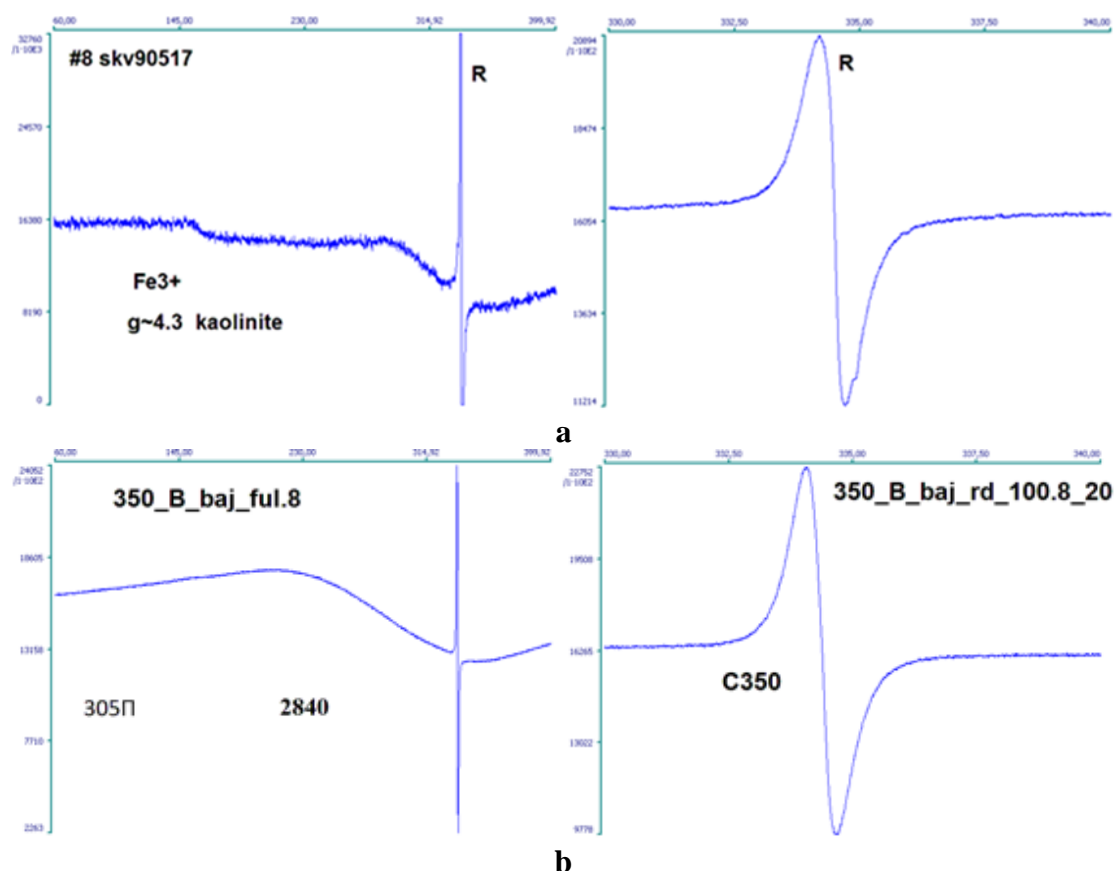


**Figure 3.** a) Features of the void space, “felt” forms of illite, the “normal” section of the Bazhenov suite; b) sample from "anomalous" section of the Bazhenov suite (sandstone - light part).

To establish the features of the distribution of organic matter and its behavior during thermal effects in samples of the “normal” and “anomalous” types of sections, laboratory studies of the samples by electron paramagnetic resonance (EPR) were carried out on a CMS8400

spectrometer 3 cm range. Experiments with samples of the Bazhenov suite were carried out at different temperatures: at room temperature and after heating for 30 minutes in an atmosphere of hydrogen at temperatures up to 350°C in a horizontal electric furnace (type SUOL).

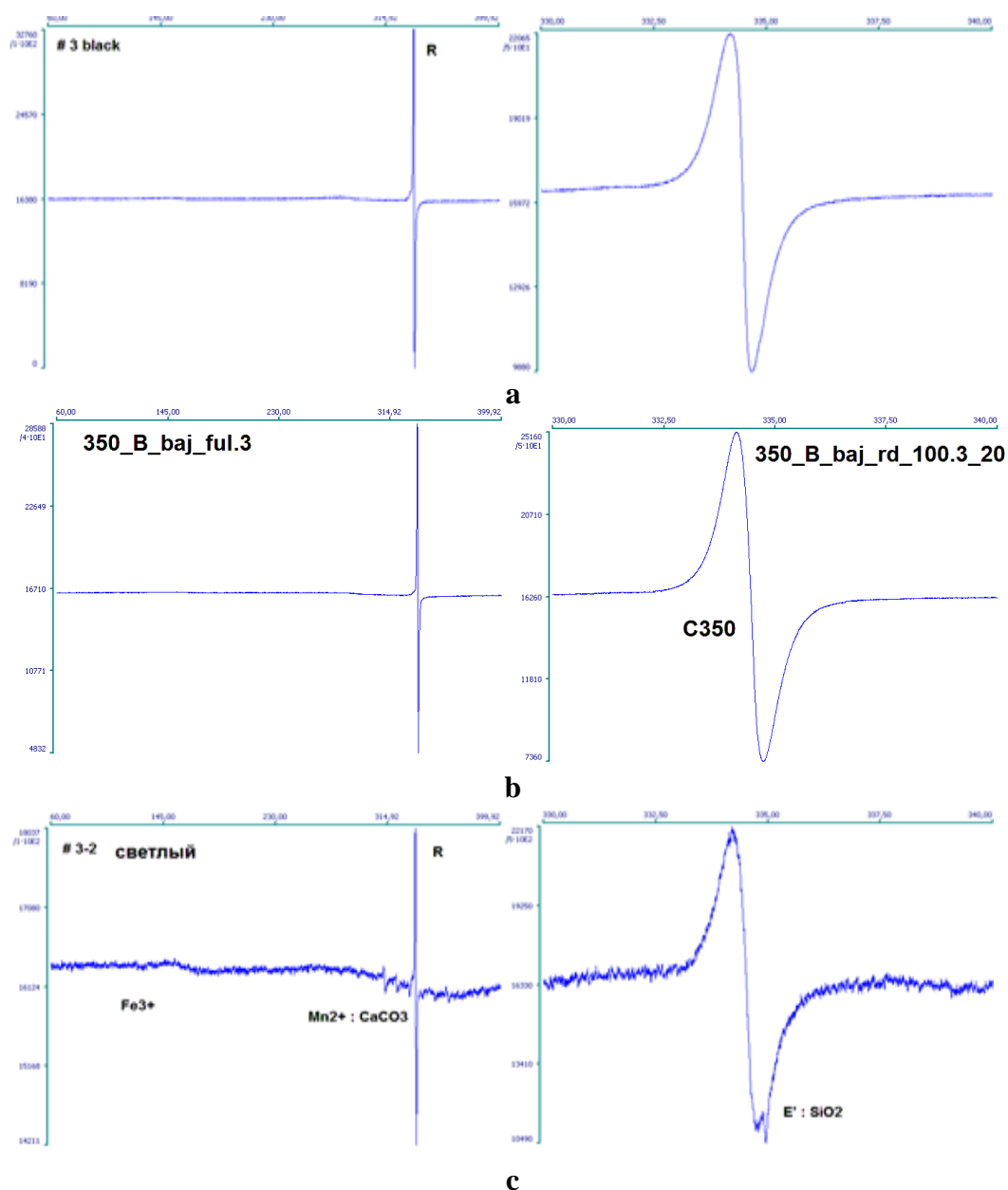
Studies show that the spectra corresponding to the samples of a “normal” section of the Bazhenov suite emit intense lines of the organic radical, E'-quartz lines, Fe<sup>3+</sup> lines and kaolinite (with  $g \sim 4.3$ ) (Figure 4a). After thermal exposure at a temperature of 350°C, the lines of the organic radical are more symmetrical and have an age intensity of the reflex, which indicates the process of pyrolysis of organic substances (Figure 4b).



**Figure 4.** Characteristic EPR Spectra – sample analysis for rocks of the “normal” section of the Bazhenov suite. a) initial sample, at room temperature; b) after thermal exposure at a temperature of 350°C.

Figure 5 shows the EPR spectra of the sample of the “anomalous” section of the Bazhenov suite; the behavior of organic matter in the light part (sandstone) and clay-argillite part (black part) was analyzed. The largest amount of organic matter in the original sample is associated with the clay-argillite part of the rocks, where the line of the organic radical is clearly distinguished (Figure 5a). At temperatures of 350°C, pyrolysis of organic matter occurs, and the intensity of line of free organic radical increases (Figure 5b). Examination of the light part

of the sample (sandstone) shows that the mineral composition of the rocks differs sharply from the black part: the lines corresponding to  $Mn^{2+}$  in calcite  $CaCO_3$ , the  $Fe^{3+}$  line and a distinct  $E'$ -quartz line are distinguished in the EPR analysis (Figure 5c). The organic radical line in the light part of the rock is less intense than the black part. After thermal impact on the sample, an increase in the intensity of the organic radical line was not observed in the EPR spectra.



**Figure 5.** Characteristic EPR Spectra – sample analysis for rocks of black and light parts of the “anomalous” section of the Bazhenov suite. a) initial sample, at room temperature (black part); b) the black part of the sample after thermal exposure at a temperature of 350°C; c) the light part at room temperature.

## Conclusions

1. The obtained results indicate that the value of the free organic radical in the rocks of the Bazhenov formation is significantly higher than that of the rocks of the Achimov formation. High values of the free organic radical indicate an increased content of organic matter in the original rock (Figure 4a).
2. In some of the studied samples, the presence of vanadium was recorded on the EPR spectra and it was noted that in samples belonging to the “normal” section of the Bazhenov suite, the content of vanadium increases with depth.
3. In order to determine the possible hydrocarbon potential of the rocks of the Bazhenov suite, studies have been conducted of the process of pyrolysis of organic matter, it was found that at a temperature of 350°C, the formation of new free hydrocarbon radicals was recorded. This indicates that the rocks of the suite in natural conditions did not fully realize their hydrocarbon potential.
4. According to the results of studies of the rocks of the Bazhenov suite, it can be concluded that the deposits of the “normal” section not only contain a large number of ready and hard to recover hydrocarbons, but also have an additional generation potential.
5. The extraction of hydrocarbons is carried out only from the “anomalous” section of the Bazhenov suite due to the clinoform complexes of the Achimov formation. Profitable extraction of hydrocarbons from the “normal” section requires more detailed study and application of new technologies for the development and production of hydrocarbons.

## Acknowledgements

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