

## ПРОБЛЕМЫ ГЕОЛОГИИ И ОСВОЕНИЯ НЕДР

NaSO <sub>4</sub> <sup>-</sup>	0.2	2.0	1.0	5.8	8.9	2.2	7.9	5.8
K+1	98.8	91.5	92.9	83.8	66.8	55.7	49.4	46.6
KCl	0.5	5.7	5.6	8.9	22.0	41.5	40.7	46.0
KSO <sub>4</sub> <sup>-</sup>	0.3	2.7	1.4	7.3	11.2	2.8	9.9	7.4
Br <sup>-</sup>	100	100	100	100	100	100	100	100
Mn <sup>+3</sup>	100	100	100	100	100	100	100	100
FA2-Fe	100	100	99.9	100	100	100	100	100
FA2-Al	99.6	99.8	99.7	99.9	99.9	100	93.8	100
H <sub>4</sub> SiO <sub>4</sub>	99.8	99.3	99.5	98.4	98.2	99.5	99.0	99.3
H <sub>3</sub> BO <sub>3</sub>	99.2	98.7	98.6	98.6	97.6	96.5	96.2	95.9
H <sub>3</sub> AsO <sub>3</sub>	99.2	99.0	99.0	99.0	98.9	99.0	99.0	99.0

Note: \* - the number of sample is given according to table 1, FA1-Me, FA2-Me - Organically complexed Me to dissolved fulvic acid. Sites 1 and 2 refer to carboxylic and phenolic functional groups, respectively.

Every type is characterized by unique chemical elements behavior, but there are some characteristics in common. For example, such elements as Si, B, As migrates in the form of H<sub>k</sub>MeO<sub>n</sub><sup>m</sup> ion; Br and Mn only in ionic form. Organic complex is predominant form for Al and Fe. Content of dissolved organic matter increases with the growth in total mineralization in a lake.

As for the major cations, ionic pattern of migration reduces with increase of mineralization, while complexes with the predominant anion increase. Thus, content of cations with carbonate ion increases in soda lakes. Content of complexes such as CaHCO<sub>3</sub> and MgHCO<sub>3</sub> increases up to 40% of the general mineralization in water, while Na, K continue accumulating in water solution. In chloride type of lakes, which are characterized by high salinity, the proportion of complexes with chloride ion is more than 50% in most cases.

Therefore, in the territory of the Kulunda Plain (Altai Territory) chloride type of lakes develop, the predominant forms of migration are the complexes containing chloride ion.

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## EPR STUDY OF HYDROCARBON GENERATION POTENTIAL OF ORGANIC-RICH DOMANIC ROCKS

D.T. Gabdrakhmanov<sup>1</sup>*Scientific advisor professor G.P. Kayukova<sup>1,2</sup>*<sup>1</sup> Kazan (Volga region) Federal University, Kazan, Russia<sup>2</sup> IOPC Kazan Scientific Center

Semiluki (domanic) sediments are widespread in the Volga-Urals Basin and stratigraphically confined to the Upper Devonian Frasnian stage [8, 5, 10, 6]. Domanic sediments are composed of bituminous siliceous-carbonate rocks with a small argillaceous admixture (5.9-13.6 %). The rocks are black and dark brown due to the high organic matter content (18-20%) [6]. Domanic sediments are analogous to oil shale. The increasing interest in them in recent years conditioned by the possibility of oil shale extraction [8, 13, 1]. A distinctive feature is that rocks along with light oil contain the organic matter as a component of rock, called kerogen [8, 12, 2].

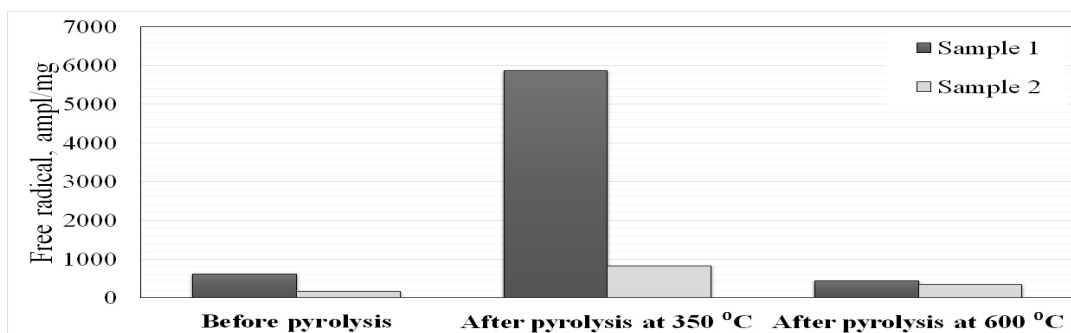
The aim of the work was to study the characteristics of the composition and structure of the mineral matrix, bitumen and kerogen, as well as the conversion of kerogen and rocks in the pyrolytic laboratory experiments using EPR spectroscopy. The objects of investigations were core materials, selected from the Domanic sediments from Berezovskaya area Romashkinskoye field. According to thermal analysis results, the substance of organic matter in the sample 1 is 35.48 %, and in the second sample is 13.36 %.

There are different methods of studying Domanic rocks to assess the prospects of the liquid hydrocarbons generation depending on the composition of organic matter in rocks and its thermal stability [11]. The special place among these methods takes the electron paramagnetic resonance (EPR) [7, 4, 3]. One of the traditional objects of EPR researches are stable free radicals – particles containing one or more unpaired electrons, so-called paramagnetic centers. Free radicals reflect the composition of carbonate and sulfate components (calcite and dolomite), show presence of organic matter, indicate ferruginization and other features of rocks composition [4, 3]. Registration of the EPR spectra of the initial rocks samples and thermally activated in the pyrolysis process was conducted on CMS-8400 X-band spectrometer at a

frequency of 9.43 GHz.

Pyrolysis conducted in hydrogen atmosphere at temperatures 350 and 600 °C for 30 minutes for each one. The first temperature is the transition point between the release of free and adsorbed hydrocarbons mode and kerogen destruction mode [2, 11]. The second temperature corresponding to the completion of thermal destruction process, due to C-C bond breaking because of the large thermal energy (thermal decomposition of kerogen). The process is accompanied by the formation of new free hydrocarbon radicals [11, 4, 3].

Content of  $Mn^{2+}$ ,  $SO_3^-$ ,  $SO_2^-$  ions, vanadyl-ion and free radicals have been estimated. There were revealed significant differences in mineralogical composition and content of organic matter in samples taken from adjacent intervals. The increasing number of free radicals was registered in all samples after pyrolysis in a hydrogen atmosphere at 350°C (Fig.). In addition to the quantitative, qualitative changes (new organic free radical  $C_{350}$ ) were registered. The research results give good reason to believe that the process of pyrolysis, to some extent, simulates the natural conditions of organic matter maturation, because content of paramagnetic centers in the organic matter increases with increasing degree of thermal maturation and sediments depth [9].



*Fig. Diagram of paramagnetic centers in organic matter content*

Pyrolysis at 600 °C is accompanied by forming a new free hydrocarbon radical  $C_{600}$ . Newly formed free radical  $C_{600}$  distinguished from  $C_{350}$  radical by smaller amplitude (Fig.). This is due to the exhaustion of the kerogen generation potential and the subsequent destruction of newly formed compounds at high temperatures.

It is suggested that Domanic source rocks have not fully realized their hydrocarbon generation potential.

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