THERMOMAGNETIC MARKERS IN STUDIES OF THE RESERVOIR ROCKS

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Thermomagnetic curves of reservoir rocks have been studied as markers of substance and reservoir rocks formation. In the temperature range of 400-530 °C it is observed an increase in the magnetization (maximum it is reached about 500 °C), then it goes the decrease in the magnetization of the newly formed magnetite, and it is sometimes visible the decrease in the magnetization of hematite (650-680 °C). The curves of the second heating differ more considerably, which depends on the content of Fe, sulfur, organic matter in samples. A series of the peaks are observed in the temperature range from 250 to 400 °C. These peaks are caused by magnetostatistical interaction of the generated pyrrhotine and magnetite. Since these minerals are formed into some aggregates, we observed temperature of Curie of pyrrhotine by the peak of the relative increase in the magnetization, caused by the transformation of magnetic and nonmagnetic sulfides into the magnetite (between 400 °C and 500 °C). This behavior is characteristic for the samples, which contain pyrite. Roughly, a quantity of pyrite can be evaluated on the decrease in the magnetization to ~400 °C. The presence of ferrous minerals, especially pyrite, not only decreases capacitive properties, but also it is the mineralogical factor, which influences the safety of the meta-stable phases of clay minerals.

INTRODUCTION

Thermomagnetic markers are connected with ferrimagnetic component, which can be fixed, also, on the spectra of the electron paramagnetic resonance in the form of wide signal. These markers are connected, first of all, with the ferric minerals, wide-spread in the rocks. They are sensitive to changes of geological medium. Therefore they can be used as the indicators of different geological processes [Sholpo, 1977]. In the sedimentary rocks the following ferric minerals of most frequently are revealed: hydroxides (more than 20 varieties of minerals), hematite, magnetite, maghemite, siderite, pyrite and a whole series of ferric sulfides, and also Fe enters into the composition of many silicates and clay minerals. The magnetic (ferro-, ferri-, antiferromagnetic) minerals of Fe are investigated by sufficiently simply magnetic methods, which reveal the characteristic thermomagnetic parameters, such as a Curie temperature, at which the substance from the ferrimagnetic state passes into the paramagnetic. There is a whole series of phase transitions of the different kind at different temperatures, which are noted by changes in the magnetic properties of minerals. The set of all thermomagnetic parameters makes it possible reliably to diagnose the very low contents of the ferric minerals, including - not only magnetic, in the sedimentary rocks. In this work thermomagnetic markers are used for studying the core of reservoir rocks. The application of these markers is useful for understanding the processes of the forming of rocks and their conversion.

OBJECT

The object of studies was the core of wells (100 samples), selected from the productive reservoirs (from the bottom zones of petroleum deposits) of the vasyuganskaya division of the Upper Jurassic the adjacent (Nivagalskoe deposit) (6 wells) and (Las-Eganskoe) (4 wells) fields, which are located in the northern part of the Nizhnevartovsky Dome of the Sredneobskaya oil and gas-bearing region. Upper Jurassic deposits are extended within entire Nizhnevartovsky Dome, being the independent regional oil and gas-bearing set of Mesozoic. At the present time the numerous petroleum deposits have been here found [1, 4].

The rocks of Vasyuganskaya division on the studied fields are the sandy-silt-clay rocks, which were being accumulated under the conditions of the open sea during the phase of the regression of Callovian- Oxford sea pond. Steeling-accumulation occurred in the extensive offshore-marine plain, in weakly differentiated the paleogeographic and facial situations with the remote regions of removal. The common thickness of the deposits of Vasyuganskaya division varies from 70-75 m in the central and eastern parts of the Nizhnevartovsky Dome to 80-90 m within the southwestern, North Western sinking. The topographical- tectonic conditions of steeling-accumulation are the basic factor, which influences changes in the values of sandiness, effective thicknesses, the physical properties of reservoir rocks.

The studied rocks are, in common, the sandstones of the upper member of Vasyuganskya division. The sandstones of productive layers are light grey, fine-grained, frequently medium-grained and silty and to different degree muddy. The sandstones are horisontally, wavily and lenticularly laminar due to the nonuniform distribution of clay, silt and plant detrital material. The sandstones are polymict. Content of quartz in them is 40-60 %, feldspar – 20-40 %, micas - from 1 to 3-4 %, the fragments of rock clastics – 10-25 %. Among the rock clastics the clay rocks, effusive, silicon-quartz rocks predominate. Authigenic minerals are pyrite, carbonate minerals, hydroxides of ferric. The average content of cement in the sandstones of productive layers 5-10 %, rarely to

20-25 %. The composition of cement is mainly clayer, composed of kaolinite, hydromica and chlorite. The thickness of sandstones varies from several meters to 15-18 m. The mean value of porosity composes 15.5 %, permeability varies from the portions of $1*10^{-3}$ mkm^2 to $25\text{-}30*10^{-3}$ mkm^2, rarely to $50\text{-}60*10^{-3}$ mkm^2.

METHODICS

Thermomagnetic analysis. In the laboratory of the paleomagnetism of Kazan State University it is developed the methodic of the estimation of the ferric and ferrous oxides and also separately - the content of pyrite content in the sedimentary rocks, based on the differential thermomagnetic analysis (DTMA) according to the inductive magnetization [3] produced on the automated installation of the controlled minicomputer. The torsion balance is sensing element of equipment. It is the thin-walled quartz lever, suspended on the thin elastic steel threads. The sample (mass of approximately 0.1 g) in the thin ceramic tube is hung up to the end of the lever. This part of the device is found in the clearance of electromagnet. In the heterogeneous magnetic field to the lever acts the force, proportional to the gradient of the strength of field and magnetic moment of sample. With the continuous heating a change in the magnetic moment of test is recorded. The heating rate can be assigned from 25 to 150 °C/min. The field strength varies from 0 to 160 kA/m, the maximum heating temperature to 800 °C. Mineralogical changes with the heatings are recorded also by the curves of reheating. In fig.1 there are represented the typical integral (upper half of graphs) and differential (lower half of graphs) thermomagnetic curves of the first (1) and repeated (2) heating. In the curve of the first heating (fig. 1-I) in the temperature range from 450 to 500 °C it is observed the increase in the magnetization (peak F), caused by the new formation (with the heating) of magnetite. Analogous peak is observed practically for all samples, for example, on fig. 1-II.

The formation of magnetite occurs both as in result of the dissociation of pyrite and also in result of the restoration of Fe because of the presence of organic matter under the high heating rates. The curve of the second heating goes substantially above, i.e., it is observed an increase of the magnetization in (I_3/I_1) times. This curve is significantly more complex. Besides the continuous increase of the magnetization (in essence, due to the restoration of ferric), one can observe the special features in the temperature range of 250-400 °C . All these processes are visible better in the differential curves. An increase of the magnetization is noted by peak A, the decrease in the temperature range of Curie of magnetite - by peak B, a series of peaks in the field C is connected with the newly formed pyrrotine, which appears, as a rule, only with the presence of pyrite in samples. The Curie temperature of pyrrotine is noted by a relative increase in the magnetization due to its magnetization in the field of magnetite, since these phases exist in the same grains. The amplitude of this peak gives information about the content of pyrite in the samples. The estimation of the general content of Fe component in the samples is produced on the paramagnetic magnetization at a temperature of 720 °C (I_2) [3, 7]. Content of Fe was estimated by ratio: Content of Fe=0.9 *I_2 , where I_2 - intensity in A/m.

The content of Fe oxides is determined by the relationship of magnetizations to heating (I_1), also, after first heating (I_3) at room temperature. In the case, when the content of ferric oxide is large (more than 40 % of the total number) the coefficient K= (I_3-I_1) of /I_3 points on share of Fe oxide in the total Fe. In the case of the low content of ferric oxide the procedure is reduced to the definition of the area of peak A or the amplitude of peak F, in this case the coefficient K is defined as the ratio of the maximum amplitude of peak F to the common amplitude at the same temperature. In the case of the very low contents of Fe oxide (less than 10 % of the total number) it can be evaluated the presence of Fe in pyrite in the arbitrary units on the amplitude of peak D.

In the systematic complex of studies besides the thermomagnetic analysis there were also used the measurements (after extracting) of open porosity (by method of saturation), absolute permeability (by pumping of air through sample), carbonate content (treatment by 10 % hydrochloric acid), granulometric composition (method of Sabanin), control determinations by X-ray diffraction method.

Granulometric composition was evaluated both according to the contents of fractions and according to average size of grains D

$$D = (\sum_{i=1}^{n} D_i p_i) / \sum_{i=1}^{n} p_i , \qquad (1)$$

where Di - average size of i-th oh fraction, p_i - content of i-th oh fraction.

The value of relative entropy, determined by the formula:

$$H = -\sum_{i=1}^{n} p_i \log p_i / \log n \qquad (2)$$

where p_i - portion (probability) of component in the n- component system.

The advantage of the use of relative entropy for evaluating the heterogeneity of the rocks consists in the presence of its upper (1) and lower (0) limits of change; therefore relative entropy gives the possibility to evaluate the significance of heterogeneity, without resorting to the comparison of the studied samples. According to [5] the samples with the relative entropy of less than 0.5 can consider homogenous, that consists of the grains of similar sizes. The value of relative entropy of more than 0.5 corresponds to the non-sorted samples. For the statistical analysis of the results of studies it was used the classification of [2]. It is the classification of distributions according to the ratio of the maximum value of massive to the mean. This relation is called the index of heterogeneity and makes it possible to classify empirical distributions according to the types, which correspond to different statistical-probability laws.

RESULTS

According to the data of granulometric analysis the average content of sandy fraction (0.1-1 mm) is respectively 72.6 % (Nivagalskoe field), 73.9 % (Las-Eganskoe field), 73.3 % (common massive). In the sandy fraction small grains with the size of 0.1-0.2 mm predominate: 39.2 % (Nivagalskoe field), 44.4 % (Las-Eganskoe field), 41.9 % (common massive). Silt (0.1-0.001 mm) fraction content is 16.3 % and 10.4 % and clayer (mud) fraction (<0.01 mm) content is 20.2 % и 5.2 % for first and second field, and 18.4 % и 7.8 % (common massive). By the granulometric composition two types of rocks have been revealed: 1. silty sandstone; 2. muddy-silty sandstone.

The integral granulometric parameters D and H were calculated for the majority of samples. Average values D are equal to 0.18 mm (Nivagalskoe field) and 0.2 mm (Las-Eganskoe field), which indicates the predominance of fine-grained fraction in the samples. Mean values of H in both fields are close and compose 0.73 (Nivagalskoe field) and 0.74 (Las-Eganskoe field). Thus, samples are heterogeneous. According to the ratio of maximum to the mean both integral parameters D and H are closely to the normal and relate to the left-asymmetric distribution.

The mean values of the parameters of species on Nivagalskoe and Las-Eganskoe fields are:

- the porosity: 14.41 % and 13.29 %;
- the absolute permeability: $27.14*10^{-3}$ mkm^2 and $17.5*10^{-3}$ mkm^2;
- the carbonate content: 5.47 % and 3.3 %.

Distribution of the

- porosity: is close to the normal, left-asymmetric;
- absolute permeability: is close to the logarithmically normal, right-asymmetric;
- the carbonate content: is close to the logarithmically normal, right-asymmetric.

It was obtained that an increase in the capacitive-filtration properties of the samples is connected with an increase in the sandiness (positive correlation of porosity and permeability with value D: for example, correlation coefficient between permeability and D is equal to 0.30 and 0.29 for both fields), also, with the decrease of carbonate content (for example, correlation coefficient between the permeability and the carbonate content it is equal - 0.48 and – 0.46) and entropy (correlation coefficient between the permeability and the entropy it is equal - 0.36 and –0.30).

Results of thermomagnetic analysis

Typical curves of thermomagnetic analysis are represented on fig. 1.

In the temperature range of 400-530 °C it is observed an increase in the magnetization (maximum it is reached about 500 °C), then it goes the decrease in the magnetization of the newly formed magnetite, and it is sometimes visible the decrease in the magnetization of hematite (650-680 °C). The curves of the second heating differ more considerably, which depends on the content of Fe, sulfur, organic matter in samples. The curve, which most vividly characterizes the processes, which take place with the reheating, is represented on the fig. 1- I.

A series of the peaks are observed in the temperature range from 250 to 400 °C. These peaks are caused by magnetostatistical interaction of the generated pyrrhotine and magnetite. Since these minerals are formed into some aggregates, we observed temperature of Curie of pyrrhotine by the peak of the relative increase in the magnetization, caused by the transformation of magnetic and nonmagnetic sulfides into the magnetite (between 400 °C and 500 °C). This behavior is characteristic for the samples, which contain pyrites. Roughly, a quantity of pyrite can be evaluated on the decrease in the magnetization to ~400 °C.

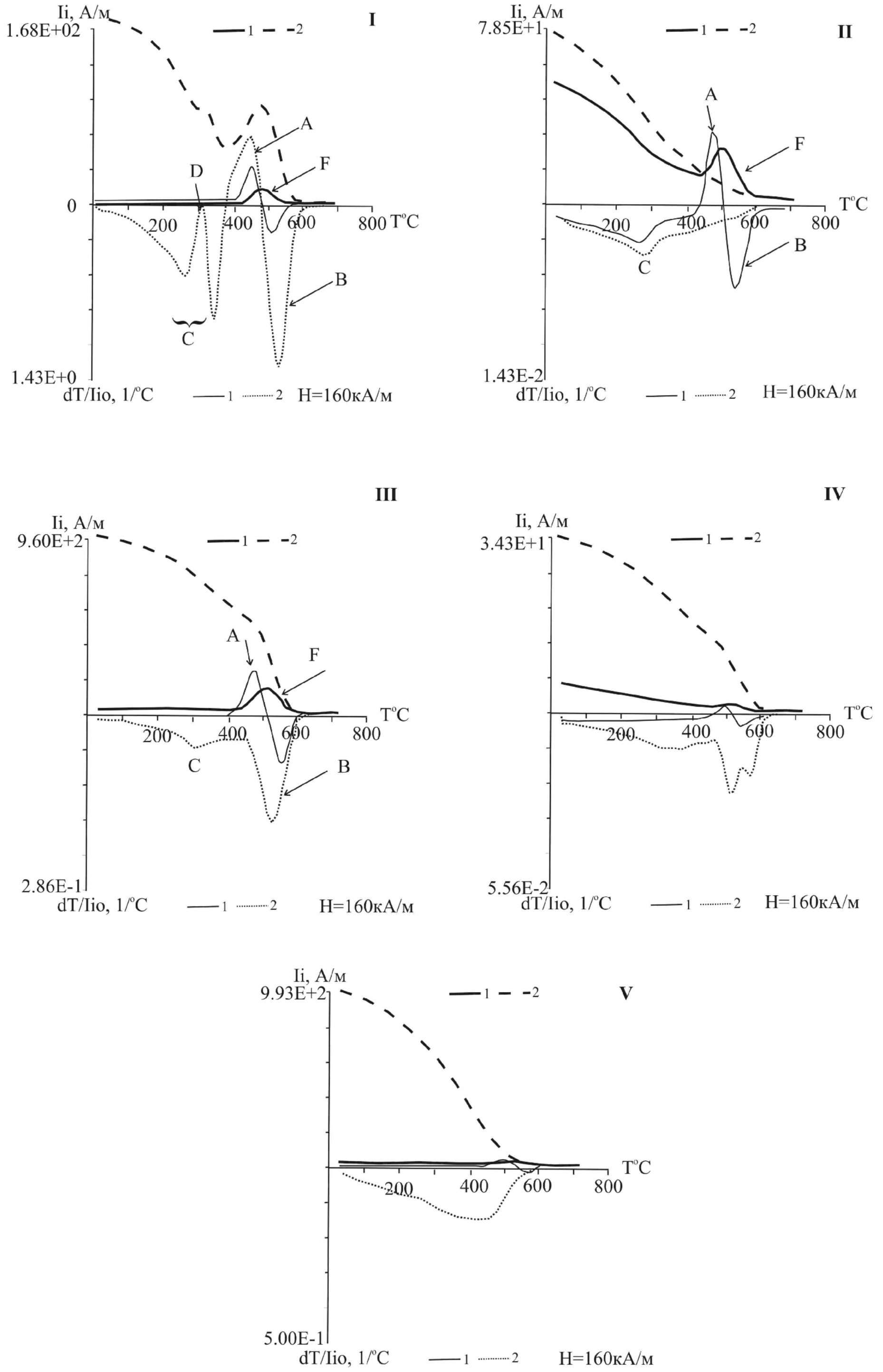

Figure 1. Typical integral (upper half of graphs) and differential (lower half of graphs) thermomagnetic curves of the first (1) and repeated (2) heating

Such behavior is revealed not in all samples. A number of mineral phases under heatings of Fe sulfides has most diverse Curie temperatures: from 280 °C on the fig.1-II to 320 °C on the fig. 1-III. In some curves it is revealed the phase with the Curie temperature ~520-530 °C (fig. 1-V). Sometimes this phase is observed in the association with the magnetite (fig. 1-IV).

Total and pyrite Fe, evaluated on the thermomagnetic curves is characterized by weakly right-asymmetric variable and right-asymmetric logarithmically normal variable nature of distribution respectively. It is established direct dependence between them (fig. 2).

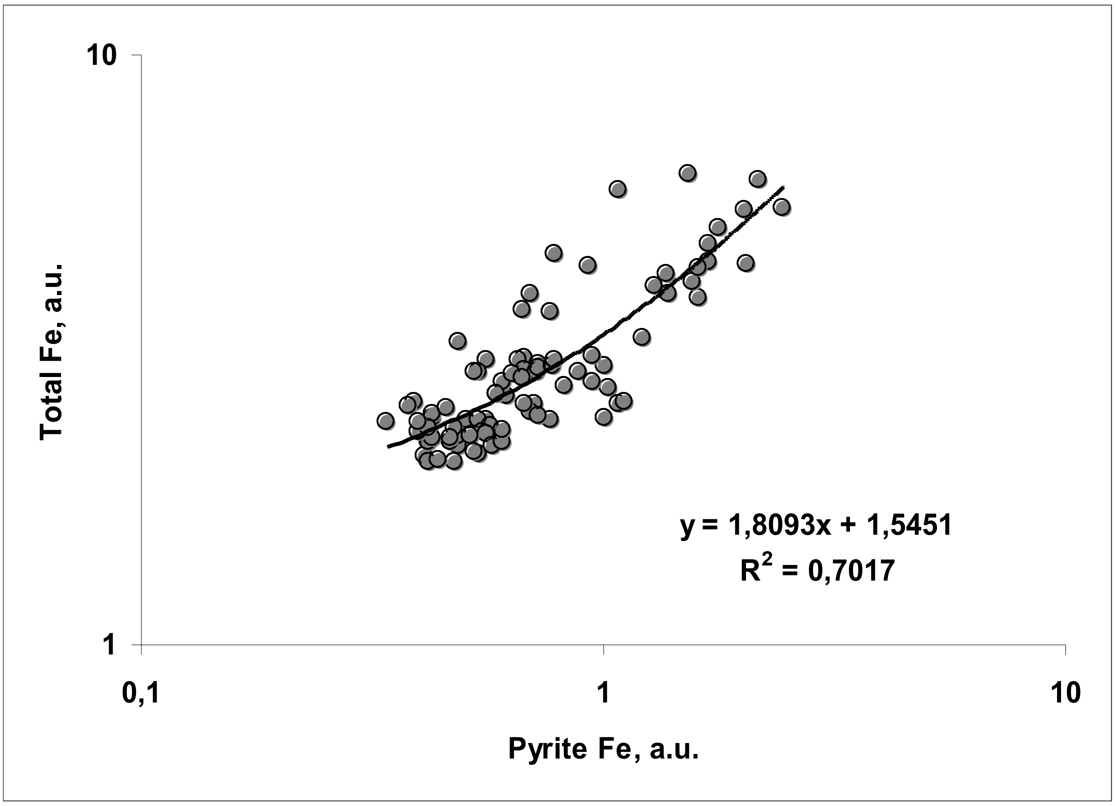

Figure 2. Relationship between total and pyrite Fe

It is revealed the tendency of porosity decreasing because of pyrite content increasing (fig. 3) which indicates that the part of the pyrite formed in a result of superimposed epigenesis.

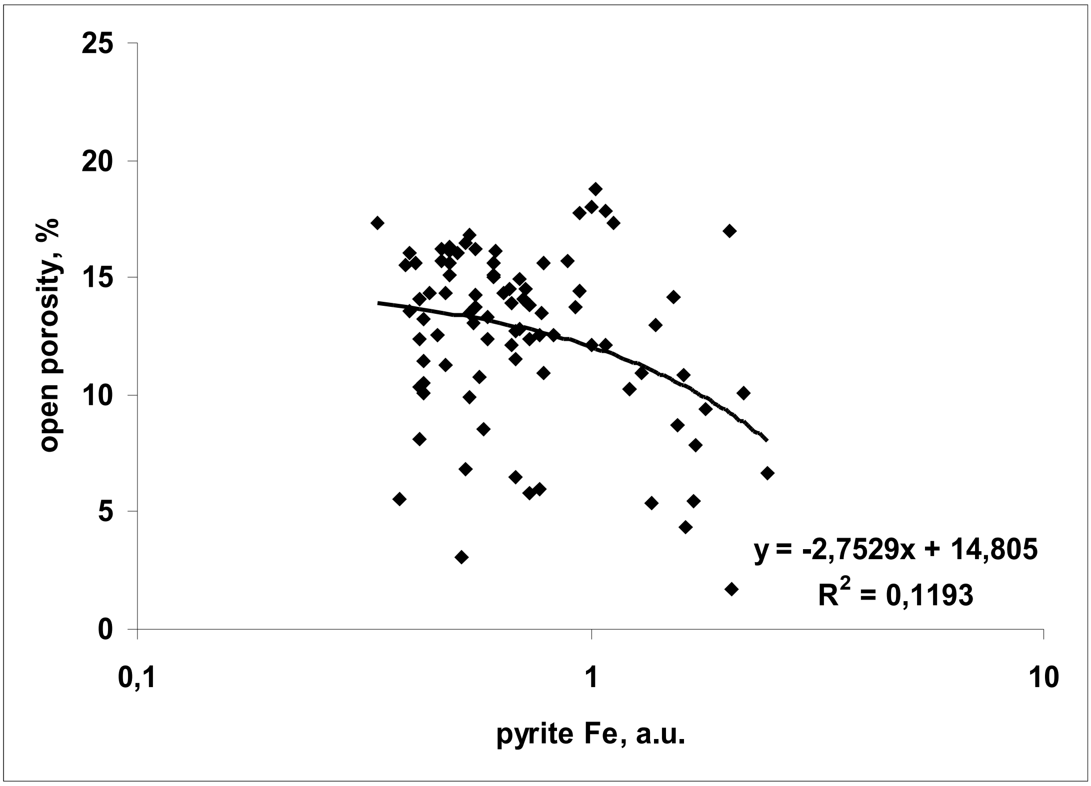

Figure 3. Relationship between open porosity and pyrite Fe

The presence of ferrous minerals, especially pyrite, not only decreases capacitive properties, but also it is the mineralogical factor, which influences the safety of the meta-stable phases of clay minerals. Actually, there are revealed the micas, been, judging by the relationship of intensities 001 reflexes, dioctahedral component. Trioctahedral component gives the regulated according to the law 1:1 (mix-layered) black mica-vermiculite (fig. 4, 5). Pyrite indicates the reducing environment, in which the clayey meta-stabile phases indicated are capable of remain. The latter are dangerous by the fact that with a change in the hydrochemical regime of reservoir, they can degrade to the mix-layered phases of montmorillonite type, whose significant content (~1 %) it can sharply decrease (~ in 10 times) the permeability of reservoir.

CONCLUSION

For the reservoir rocks with the established mineralogical characteristics it should be with the caution selected the water for the pumping. For example, pumping into such reservoir of the heated Caspian water can lead to emergency reduction in the pick-up of the injection wells because of the formation of clay phases of montmorillonite type.

The complex of thermomagnetic markers with the X-ray diffraction definitions is useful tool for the revealing of pyritization not only as the factor of the seal of the hydrocarbon deposits, but also as the factor, which conserves the metastable clay phases, which with a change in hydrochemical environment, can degrade and "seal up" filtration channels in reservoir rocks.

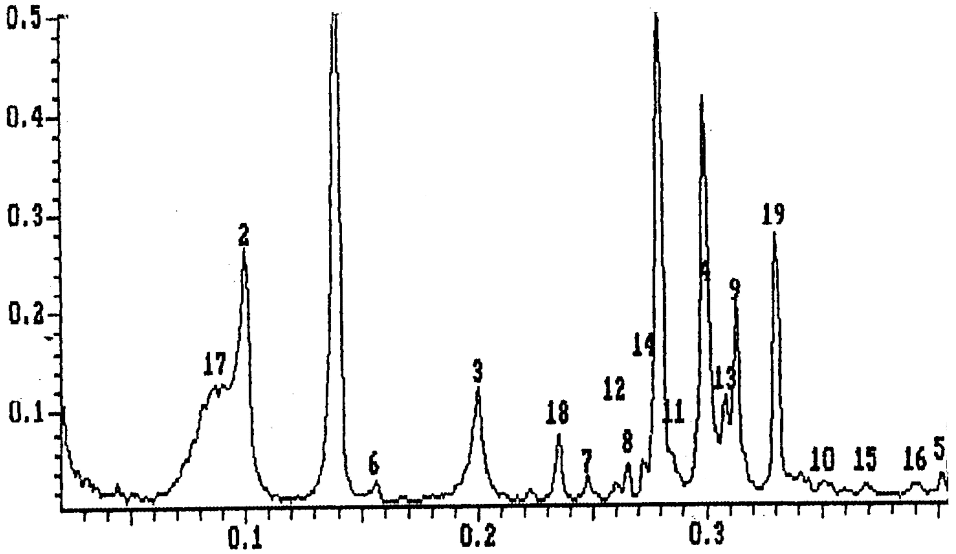

Figure 4. X-ray diffraction diagram of clayey component in sandstone (dry probe)

n	***D(A)***	***Mineral name and hkl***	***I/I_0***
0	*7.196*	*Kaolinite 001n*	*1.00*
1	*3.584*	*Kaolinite 002n*	*0.93*
2	*10.020*	*Micas-di 001n*	*0.35*
3	*4.999*	*Micas-di 002n*	*0.16*
4	*3.337*	*Micas-di 003n*	*0.29*
5	*2.497*	*Micas-di 004n*	*0.05*
6	*6.428*	*Labr-albite-low*	*0.03*
7	*4.046*	*Albite-high-low*	*0.03*
8	*3.772*	*Albite-high-low*	*0.06*
9	*3.196*	*Albite-high-low 020*	*0.26*
10	*2.856*	*Albite-high-low 131*	*0.03*
11	*3.500*	*Albite-low*	*0.10*
12	*3.859*	*Microcline-max 130*	*0.13*
13	*3.244*	*Microcline-max 040*	*0.14*
14	*3.671*	*Hematite 102*	*0.19*
15	*2.712*	*Hematite 104*	*0.03*
16	*2.565*	*Ferrihydrite*	*0.03*
17	*11.557*	*Chlor-verm 1:1 600*	*0.17*
18	*4.263*	*Quartz-low 100*	*0.10*
19	*3.029*	*Calcite*	*0.37*

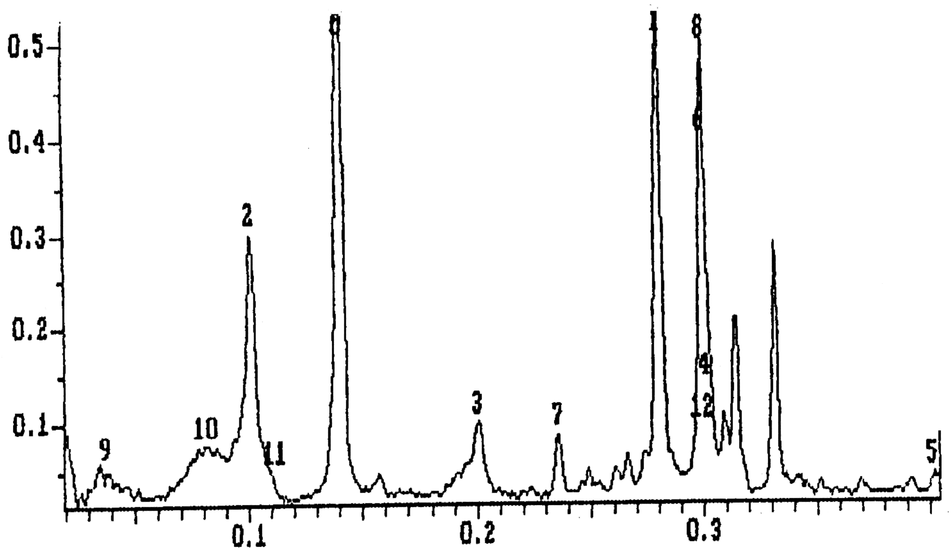

Figure 5. X-ray diffraction diagram of clayey component in sandstone (probe saturated by ethylene-glicol)

n	***D(A)***	***Mineral name and hkl***	I/I_0
0	*7.156*	*Kaolinite 001n*	*1.00*
1	*3.57*	*Kaolinite 002n*	*1.00*
2	*9.950*	*Micas-di 001n*	*0.56*
3	*4.993*	*Micas-di 002n*	*0.17*
4	*3.332*	*Micas-di 003n*	*0.24*
5	*2.497*	*Micas-di 004n*	*0.06*
6	*3.34*	*Illit-mont-D-EG*	*0.75*
7	*4.245*	*Quartz-low 100*	*0.14*
8	*3.34*	*Quartz-low 101*	*0.93*
9	*26.812*	*Biot-verm-0-1:1 EG*	*0.08*
10	*12.146*	*Biot-verm-0-1:1 EG*	*0.12*
11	*8.997*	*Biot-verm-0-1:1 EG*	*0.07*
12	*3.34*	*Biot-verm-0-1:1 EG*	*0.16*

REFERENCES

1. Balin V.P., Medvedskiy R.I., Nesterov I.I., Brekhuntsov A.M., Khafizov F.Z., Fedortsov V.K. Features of prospecting and expoitation of different deposits types of West Siberia // Geology of oil and gas. - 1989. - №6. - P.2-10. (in Russian)

2. Bogatskiy V.V. The mathematical analysis of prospecting network. - M.: Gosgeoltekhizdat, 1963. (in Russian)

3. Burov B.V., Nurgaliev D.K., Yassonov P.G. Paleomagnetic analysis. - Kazan: Kazan State University, 1986. (in Russian).

4. Kontorovich A.E., Nesterov I.I., Salmanov F.K. Geology of oil and gas of West Siberia. - M.: Nedra. - 1976. (in Russian)

5. Logvinenko N.V. Petrography of sedimentary rocks. – M.: Vysshaya shkola, 1984 (in Russian)

6. Sholpo L.E. The use of magnetism of the rocks for the solution of geological problems. - L.: Nedra, 1977. (in Russian)

7. Vonsovskiy S.V. Magnetism. - M.: Science, 1971. (in Russian)