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STUDY OF THE EFFECT OF HYDROCARBONS ON MAGNETIC CHANGES IN SOILS (AZERBAIJAN)

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Summary. The paper examines the observed changes in magnetic minerals exposed to hydrocarbons. The purpose of the magnetometric study was to identify the relationship between magnetic parameters and manifestations of oil-bearing formations. The oldest oil field, which is located on Pirallahi Island, was chosen as a control object for the study. We studied the magnetic parameters of samples from both sites to compare the magnetic parameters of soils from the Pirallahi oil field with soils not affected by the influence of hydrocarbon fluids from the Dubendi site. As a result of studying the magnetic parameters, it was found that some magnetic parameters of the Pirallahi oil field are hundreds (or more) times higher than those of the Dubendi area. Both magnetic and chemical studies of the studied soil samples have shown the presence of magnetic minerals: magnetite and hematite. The carrier of magnetization is magnetite on the Pirallahi oil field. The magnetic mineral is hematite for the Dubendi region. Thus, as a result of the petromagnetic studies and chemical analyses, the reason for the observed increase in the magnetic signal over the Pirallahi oil field was identified. In the studied soils of the Pirallahi oil field, the magnetite grains found belong to the fine-grained magnetic fraction. In the Dubendi area, which is not affected by hydrocarbon impact, finely dispersed hematite was found as a magnetization carrier.

Keywords: *petro magnetism, soil magnetism, hydrocarbons, Pirallahi Oil Field*

Introduction

In recent decades, numerous scientific papers have been published indicating that oil and gas reservoirs can be detected using micro-magnetic methods. The micro-magnetic method consists of a combination of high-resolution magnetic surveys (Gadirov, 2013) with detailed rock-magnetic examination of sediments and soils to detect changes in magnetic and iron-bearing minerals caused by hydrocarbon seepage (Badejo, 2021; Benthien and Elmore, 1987; Foote, 1992; Ellwood and Burkart, 1996; Liu et al., 1998a; Liu et al., 1998b; Liu and Liu, 1999; Goldhaber and Reynolds, 1991). Magnetic studies (Elmore et al., 1987; Elmore and Crawford, 1990) indicate a genetic relation between hydrocarbon migration and the precipitation of authigenic magnetite.

Magnetic minerals are formed or changed in the presence of hydrocarbons. Near-surface samples of soils and sandstones from oil and gas fields (Díaz et al., 2000; Abdulkarim et al., 2022; Aldana et al., 2003; Costanzo-Alvarez et al., 2006; Emmerton et al., 2013) revealed the presence of authigenic magnetite in them. On the other hand, when studying near-surface samples of soils and sandstones where there are no oil and gas deposits (i.e., accumulations of hydrocarbons), the presence of any magnetite has not been revealed. Magnetic exploration work carried out in areas of oil and gas fields recorded abnormal magnetic field signals (Donovan et al., 1979; Gadirov, 2013).

Hydrocarbons do not have significant magnetic properties capable of causing a geomagnetic field anomaly over oil and gas reservoirs. The cause of Such anomalies is the appearance of newly formed magnetic and iron-containing minerals in soils and sandstones under conditions of hydrocarbon seepage (Benthien and Elmore, 1987; Saunders et al., 1991; Foote, 1992; Ellwood and Burkart, 1996; Goldhaber and Reynolds, 1991; Liu and Liu, 1999; Liu et al., 1998a; Guliyev et al., 2003). Magnetic methods can be used for additional oil and gas exploration and prospecting.

As noted, hydrocarbon reservoirs are often associated with prominent magnetic anomalies, presumably caused by diagenetic alteration of magnetic and other iron-bearing minerals in hydrocarbon (oil) seepage environments. However, the mechanisms and pathways of hydrocarbon-induced magnetic changes remain poorly understood, making it difficult to develop reliable magnetic-based exploration and environmental monitoring methods. As it is known, hydrocarbons do not have magnetic properties capable of causing a magnetic anomaly over an oil and gas reservoir. The question is: where does the source of the anomaly come from? The reason is the interaction of seeping hydrocarbon fluids with rocks encountered on the migration route.

Today, we know three mechanisms that explain the formation of the secondary magnetic minerals that develop in a hydrocarbon environment due to the seepage of hydrocarbon fluids. The first model describes diagenetic changes in magnetite. This model was first proposed by Donovan et al. (1979) based on aeromagnetic surveys at the Cement oil field in the Anadarko Basin, Oklahoma. They suggested that diagenetic magnetite forms as a result of seeping hydrocarbons. Diagenetic magnetite occurs through the substitution of Fe^{3+} from hematite for Fe^{2+}. In the second model, a more significant role is likely played by changes in pyrite. According to Pirson (Pirson, 1982), the location of oil and gas reservoirs is determined using the induced polarization (IP) method, which is based on pyrite changes. Research by Reynolds et al. (1990a, 1990b) and Goldhaber and Reynolds (1991) examines the relationship between microseepage of hydrocarbons and iron sulfide minerals. They believe that pyrrhotite causes the magnetic anomalies. They argue that pyrite (FeS_2), which forms in large quantities due to hydrocarbon seepage, adheres to pyrrhotite creating an abnormal magnetic signal. A third model, which explains the formation of an abnormal magnetic signal focuses on siderite (iron carbonate). In a hydrocarbon environment, siderite formation is widespread. This process increases rock magnetization, which can be useful in paleomagnetic studies (Reynolds et al., 1990a; Elmore and Crawford, 1990).

Due to its variable valence, iron, which is part of finely dispersed oxides and hydroxides, can participate in various chemical reactions. In particular, iron, which is part of finely dispersed oxides and hydroxides, can be reduced. Sedimentary rocks containing iron oxides and hydroxides can reduce iron oxides and hydroxides when exposed to fluids of migrating hydrocarbons. These reducing geochemical reactions lead to new iron-containing compounds with magnetic properties.

Scientific studies have shown that hydrocarbon deposits are often associated with noticeable magnetic anomalies, which may be caused by diagenetic changes in magnetic and other iron-containing minerals under conditions of hydrocarbon seepage. However, the mechanisms and pathways of magnetic changes caused by hydrocarbons remain poorly understood, which prevents the development of reliable monitoring methods based on magnetic measurements.

Thus, it is possible to determine the migration routes and accumulation zones of hydrocarbons using petromagnetic and magnetic-mineralogical data of the studied soils and sandstones. Petromagnetic studies are a potential magnetic proxy for determining hydrocarbon migration routes. In addition, this useful data on the magnetic properties of hydrocarbon-exposed soil and sandstone samples will allow determining the (surface) contours of oil and gas reservoirs in the Earth's crust.

Comprehensive studies (Abdulkarim et al., 2022; Aldana et al., 2003; Benthien and Elmore, 1987; Donovan et al., 1979; Elmore et al., 1987; Elmore and Crawford, 1990; Gadirov, 2013; Gadirov et al., 2023; Goldhaber and Reynolds, 1991; Perez-Perez et al., 2011; Saunders et al., 1991; Yuan et al., 2018, etc.) of magnetic fields conducted over oil and gas reservoirs, as well as rock magnetic studies (Emmerton et al., 2013; Liu et al., 1998a; Liu and Liu, 1999; Liu et al., 1998b; Menshov et al., 2015; Menshov et al., 2016; Novruzov et al., 2023a; Новрузов и др., 2023b; Novruzov et al., 2022a; Novruzov və b., 2022b; Orlyuk et al., 2018, etc.) of soil (rock) sampled directly from the areas of oil and gas fields, make it possible to improve understanding of the nature of the anomalous behavior of the geomagnetic field over hydrocarbon deposits. Further researches related to the study of the influence of hydrocarbons on the magnetic properties of soils (host rocks) and how this influence changes the magnetic and mineralogical composition of the properties of soils (host rocks) will make a significant contribution to understanding the essence of the process.

Rock Magnetic Measurements

Field measurements and sampling

As a control object of the study, the territory of the Pirallahi oil field was chosen. The Pirallahi Island is located on the eastern side of the Absheron Peninsula at a distance of about 50 km from the city of Baku (Fig. 1). The Pirallahi oil field has been in operation for over a hundred years. Crude oil is still being extracted from this oldest field today.

We studied the magnetic properties of oil-saturated soils and sandstones from the Pirallahi oil field. The study was aimed at identifying the changes in magnetic minerals in oil-saturated soils and sandstones exposed to hydrocarbon fluids.

At the Pirallahi oil field, samples were taken from depths of 0-0.5 m (from the earth's surface) from 10 points for magnetic studies (Fig. 2 and Fig. 3). At each sampling point, magnetic susceptibility was measured *in situ*. At the hydrocarbon-free Dubendi site (Fig. 2), magnetic susceptibility was also measured *in situ*.

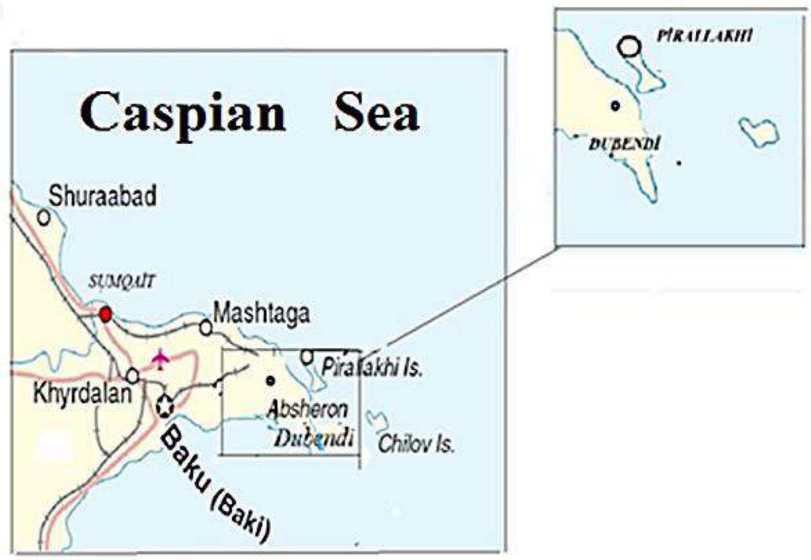

Fig. 1. Location of the study areas on Pirallahi Island and in the ecologically clean the Dubendi region

Fig. 2. Sampling locations at the Pirallahi oil field (samples 1-10) and at the ecologically clean Dubendi area (samples 11-13)

Samples were also taken from the Dubendi area for magnetic studies in the laboratory of the institute. By a pre-developed scheme, rock samples (with CPS determination) were taken near the operating oil wells. The sampled soil specimens were placed in special non-magnetic plastic containers. Each plastic container was labeled and corresponded to one sampling location.

Laboratory magnetic research

The sampled soil specimens were then taken for laboratory magnetic measurements. Such magnetic parameters as the natural remnant magnetization NRM (I_n) and the volumetric magnetic susceptibility (k) were measured in laboratory conditions. Further, various types of induced magnetizations were created. The induced magnetizations of various types were then demagnetized using alternating magnetic field techniques and a gradual temperature increase. Due to the laboratory experimental procedures, the values of isothermal remnant magnetization IRM and saturation isothermal remnant magnetization SIRM, total temperature remnant magnetization TRM, and alternative remnant magnetization ARM were obtained and measured. In the course of laboratory work, temperature demagnetization curves and curves of demagnetization by an alternating magnetic field were constructed. In addition, the ratios of the values of various types of induced magnetizations were calculated.

Thermomagnetic curves show the magnetic phase of a mineral and provide data on the changes that occur during heating. For example, chemical remagnetization can promote the formation of goethite or the transformation of hematite into magnetite. IRM measurements allow the separation of ferrimagnetic phases. The IRM method provides reliable data on the separation of ferromagnetic phases. Minerals with the same coercivity often have different unblocking temperatures. According to the Lowrie test (Lowrie, 1990), three different components of saturation magnetization are acquired by the sample: in the Z direction – 1 T, then in the Y direction by applying a field of 0.4 T, and in the X direction – 0.12 T. Thermal cleaning of the sample will isolate these components and interpret them in terms of the temperature range at which each component loses its magnetization.

As iron ions of certain groups of minerals can migrate from one crystal lattice to another, these minerals are susceptible to diagenetic oxidation (Ozdemir et al., 1993; Liu and Liu, 1999). The minerals containing iron oxides include magnetite, maghemite, and hematite. The group of oxyhydroxides includes goethite, ferrihydrite, and lepidocrotite. The group of sulfites includes greigite and pyrrhotite.

Magnetic Analysis

Magnetic studies were conducted at the Institute of Geology and Geophysics of the Ministry of Science and Education of the Republic of Azerbaijan. Several types of measurements were carried out: 1) measurement of the volume (bulk) magnetic susceptibility k; 2) measurement of the dependence of the isothermal remnant magnetization on the effect of the applied direct magnetic field (in fields from 2 to 700 A/m in 20 steps; 3) measurement of the temperature dependence of the isothermal remnant magnetization from 20°C to 800°C (measurements were carried out in the range from 20°C to 800°C under atmospheric conditions); 4) measurement of the following parameters of magnetic hysteresis: isothermal saturation remnant magnetization (Mrs), coercive force (Hc) and coercive force of remnant magnetization (Hcr). We have obtained data that will be used to create distribution maps of magnetic susceptibility and other magnetic parameters to assess the dependence of magnetic changes on the distance of the hydrocarbon reservoir.

The remnant magnetization was measured using a high-precision JR-6 instrument (Agico, Czech Republic). The measurement range of this device exceeds 11 levels (10^{-6}–10^{4} A/m). For the creation of thermo-remnant magnetization (TRM), the MMTD 24 thermal furnace (UK) was used-fully automated with high-precision temperature control. For the creation of isothermal saturation remnant magnetization (SIRM), a PAM1 magnetizer (Agico, Czech Republic) was used. A LDA5 device (Agico, Czech Republic) was used to create alternative remnant magnetization (ARM).

A rotary two-component thermo-magnetometer designed by Burakov-Vinogradov (Institute of Earth Physics, Russia) was used for magnetic and mineralogical analyses of the studied rocks. Thermomagnetic demagnetization of the studied sample was carried out using this device. Based on the course and shape of the thermomagnetic demagnetization curves, both the component composition of magnetic minerals in the sample and the possible newly formed magnetic mineral during heating were determined.

Results and discussion

Demagnetization curves in an alternating magnetic field of induced magnetizations of SRM, TRM, and ARM were plotted and analyzed. The induced acquired SRM, TRM, and ARM curves were also analyzed. In addition, the NRM/ARM and TRM/TRM ratios were calculated.

The obtained data on the magnetic data of the studied samples identifies the most sensitive magnetic parameters (or their ratios) that reflect the oil saturation of the rocks. Using these parameters, we estimate the area where oil-saturated rocks are distributed and thereby outline the contours of the oil and gas reservoirs located in the Earth's crust.

In point 1, soil specimens were sampled from the surface. At a depth of 30 cm at the same point, sandstone was sampled. The volume magnetic susceptibility of a soil sample taken from the surface is $k = 0.74 \times 10^{-3}$ SI units, at a depth of 10 cm, $k = 0.26 \times 10^{-3}$ SI units, and at a depth of 30 cm, $k = 0.31 \times 10^{-3}$ SI units. The second sampling point is approximately 50-60 m north of the first sampling point. Magnetic susceptibility of the soil at the second sampling point: from the surface is equal to $k = 0.17 \times 10^{-3}$ SI units, from a depth of 15 cm $k = 0.09 \times 10^{-3}$ SI units, and from a depth of 40 cm $k = 0.10 \times 10^{-3}$ SI units. At the third sampling point, on the surface, the soil samples have a volume susceptibility $k = 12 \times 10^{-3}$ SI units, at a depth of 10 cm, $k = 4.68 \times 10^{-3}$ SI units. It can be said that around this sampling point of approximately 50×100 m^2, the volumetric magnetic susceptibility values are quite high. The fourth soil specimen was sampled in the area of well No. 249. At the surface, the volume magnetic susceptibility was $k = 0.60 \times 10^{-3}$ SI units.

The fifth soil specimen point was selected in the northwestern part of the Pirallahi oil field. On the surface, $k = 2.15 \times 10^{-3}$ SI units, at a depth of 10 cm, $k = 3.4 \times 10^{-3}$ SI units, at a depth of 30 cm, $k = 6.33 \times 10^{-3}$ SI units. In the northern direction of the soil and sandstone sampled specimens, the volume magnetic susceptibility. The volumetric magnetic susceptibility of the samples gradually decreased as they moved towards borehole No. 1039 at 30-40 m from sampling point 5.

Fig. 3. Schematic location of soil sampling points in the study area: sampling points are indicated by black circles

The volume magnetic susceptibility of the soil measured on the surface at sampling point 6 was $k = 1.88 \times 10^{-3}$ SI units, and at a depth of 15 cm, $k = 0.24 \times 10^{-3}$ SI units.

At sampling point 7, the volume magnetic susceptibility of the soil measured on the surface was $k = 0.26 \times 10\text{-}3$ SI units at a depth of 15 cm $k = 0.48 \times 10\text{-}3$ SI units, and a depth of 30 cm $k = 0.08 \times 10^{-3}$ SI units.

Volume magnetic susceptibility of the soil measured on the surface at sampling point 8 on the surface $k = 0.36 \cdot 10^{-3}$ SI units, at a depth of 15 cm $k = 0.06 \times 10^{-3}$ SI units.

Sampling point 9 had a volumetric magnetic susceptibility on the surface $k = 1.90 \times 10^{-3}$ SI units, at a depth of 15 cm $k = 2.75 \times 10^{-3}$ SI units. At a depth of 20 cm, the volumetric magnetic susceptibility $k = 0.58 \times 10^{-3}$ SI units.

At sampling point 10, the volume magnetic susceptibility $k = 4.26 \times 10^{-3}$ SI units on the Earth's surface.

A local map of changes in volumetric susceptibility of soils is shown in Fig. 4.

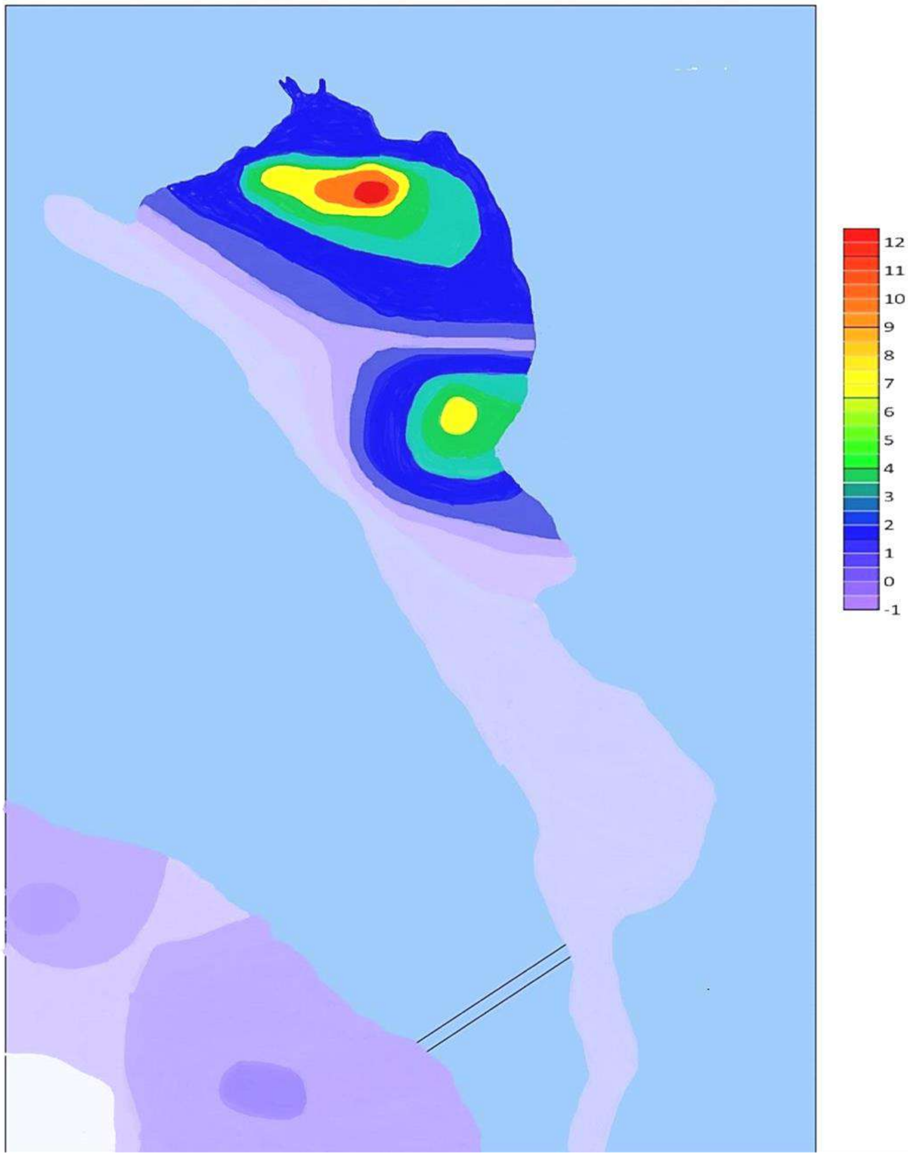

Fig. 4. Change in magnetic susceptibility of soils in the study area of the Pirallahi and Dubendi (color scale is indicated in units of 1×10^{-3}SI units)

Large accumulations of the secondary magnetite formations can explain the anomalous values of k at sampling points 3 and 5. At point 5, the observed increase with depth in the volume magnetic susceptibility (at the surface $k = 2.15\times10^{-3}$ SI units, at a depth of 10 cm $k = 3.4\times10^{-3}$ SI units, and at a depth of 30 cm $k = 6.33\times10^{-3}$ SI units) can be explained by the proximity of the paths (microcracks) along which the leaking (percolating through) hydrocarbon fluids affected the formation of new secondary magnetite minerals. This assumption is confirmed by chemical analysis of soil and sandstone samples conducted at the Analytical Center of the Institute of Geology and Geophysics. In addition, the conducted thermomagnetic analysis (Fig. 5) of the samples indicates the secondary magnetite formations at the oil field under study.

To compare the effect of hydrocarbon seepage on the formation and change of magnetic minerals in the studied area of the Pirallahi oil field, we sampled soil specimens from both Pirallahi Island and the ecologically clean Dubendi area near the island. The volume magnetic susceptibility of samples from the Dubendi area was also measured in the field. They were packed in plastic non-magnetic containers for petromagnetic researches in the Institute of Geology and Geophysics of the Ministry of National Economy of the Council of Ministers, Baku, Azerbaijan.

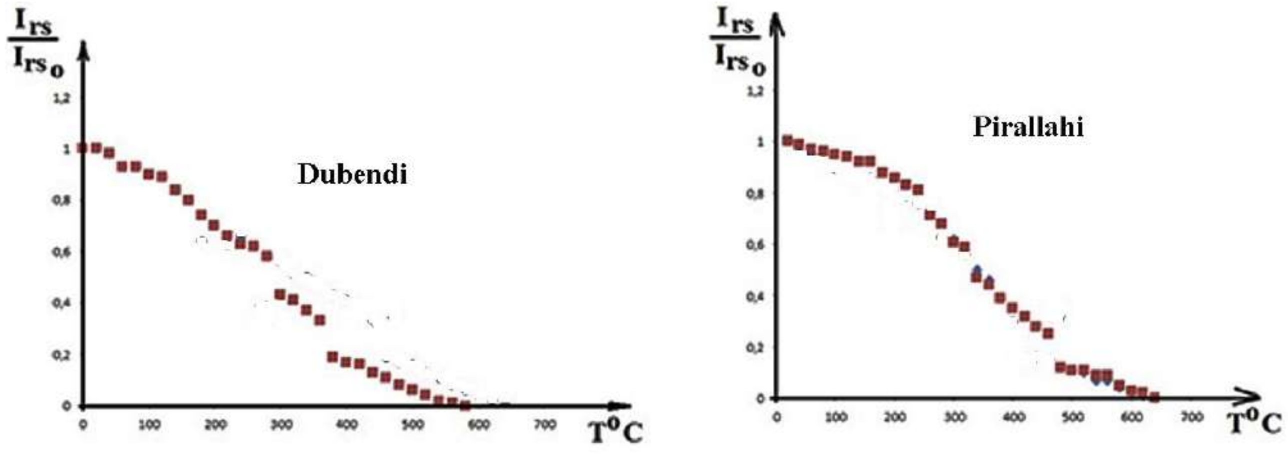

Fig. 5. Thermomagnetic demagnetization curves of soil samples from the Pirallahi and Dubendi regions

The I_{rs} (T) curves determined the Curie point of the studied rocks. The saturation isothermal remnant magnetization (SIRM) curves of temperature dependence were analyzed for all sampled soil specimens. At the Pirallahi oil field, based on the results of thermomagnetic analysis, it was established that magnetite is the carrier of magnetization. At the Dubendi site, which is unaffected by hydrocarbon influence, hematite is the carrier of magnetization (Fig. 5). Typical temperature demagnetization curves are shown in Fig. 5. As we can see in Fig. 5 for the Dubendi area, the temperature demagnetization curve of the samples has an almost linear demagnetization curve up to the Curie point equal to 625°C. Such a curve with Tc = 625°C may indicate a spectrum of finely dispersed hematite-blocking temperatures (Авилова и др., 1978). This assumption is confirmed by the fact that the Curie point of fine-grained hematite (To=625°C) is significantly smaller than the Curie point of coarse-grained hematite (Tc=675°C) (Новрузов и др., 2023b).

The isothermal remnant magnetization (IRM) was acquired in increments of 20 mT. The IRM acquisition curve is shown in Fig. 6. Progressively increasing magnetic fields applied to samples revealed two types of magnetic minerals. One of them becomes saturated at an applied field of 200 mT. A magnetic mineral that reaches saturation in a 200 mT field indicates the presence of magnetite. In the other case, the magnetic mineral saturates in a 1000 mT field, indicating the presence of hematite in the studied sample. The Curie point of 625-635°C corresponds to fine-grained hematite (Fig. 6). The isothermal remanent magnetizations, reaching saturation fields of 200 mT and 1000 mT, correspond to magnetite and fine-grained hematite, as shown in Fig. 6. Thus, the results of the progressive magnetization of samples to saturation magnetization confirmed the results of the thermomagnetic analysis.

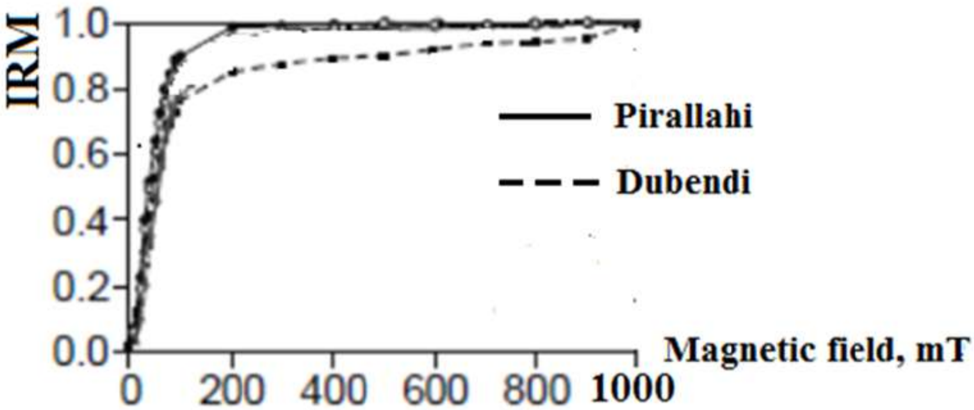

Fig. 6. Curves of stepwise isothermal magnetization of samples up to saturation from the Pirallahi and Dubendi regions

Conclusions

Magnetic studies conducted at the Pirallahi field revealed the influence of hydrocarbons on the change and appearance of new magnetic minerals in the soil and sandstones of the studied territory of the Pirallahi oil field. As a result of the interaction of oil-hydrocarbon fluids with the soils and sandstones, new secondary magnetite minerals were formed, which caused an anomalous signal in the area impregnated with hydrocarbons.

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ИЗУЧЕНИЕ ВЛИЯНИЯ УГЛЕВОДОРОДОВ НА МАГНИТНЫЕ ИЗМЕНЕНИЯ В ПОЧВАХ (АЗЕРБАЙДЖАН)

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Резюме. В статье рассматриваются наблюдаемые изменения в магнитных минералах, подвергшихся воздействию углеводородов. Целью магнитометрического исследования было выявление взаимосвязи между магнитными параметрами и проявлениями нефтеносных пластов. В качестве контрольного объекта для исследования было выбрано старейшее нефтяное месторождение, расположенное на острове Пираллахи. Чтобы сравнить магнитные параметры почв с нефтяного месторождения Пираллахи с почвами, не подверженными воздействию углеводородных флюидов с участка Дюбенди, мы изучили магнитные параметры образцов с обоих участков. В результате изучения магнитных параметров было установлено, что некоторые магнитные параметры нефтяного месторождения Пираллахи в сотни (или более) раз превышают таковые в районе Дюбенди. Как магнитные, так и химические исследования изученных образцов почвы показали наличие магнитных минералов: магнетита и гематита. Для нефтяного месторождения Пираллахи носителем намагниченности является магнетит. Для региона Дюбенди магнитным минералом является гематит. Таким образом, в результате петромагнитных исследований и химических анализов была выявлена причина наблюдаемого увеличения магнитного сигнала над нефтяным месторождением Пираллахи. В исследованных почвах нефтяного месторождения Пираллахи обнаруженные зерна магнетита относятся к мелкозернистой магнитной фракции. В районе Дюбенди, который не подвержен воздействию углеводородов, в качестве носителя намагниченности был обнаружен мелкодисперсный гематит.

Ключевые слова: *петромагнетизм, почвенный магнетизм, углеводороды, нефтяное месторождение Пираллахи*

KARBOHİDROGENLƏRİN TORPAQLARDA MAQNİT DƏYİŞİKLİKLƏRİNƏ TƏSİRİNİN ÖYRƏNİLMƏSİ (AZƏRBAYCAN)

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Xülasə. Məqalədə karbohidrogenlərə məruz qalan maqnit minerallarında müşahidə olunan dəyişikliklər araşdırılır. Maqnitometrik tədqiqatın məqsədi maqnit parametrləri ilə neft yataqlarının təzahürləri arasındakı əlaqəni müəyyənləşdirmək idi. Tədqiqat üçün nəzarət obyekti olaraq Pirallahı adasında yerləşən ən qədim neft yatağı seçildi. Pirallahı neft yatağından torpaqların maqnit parametrlərini Dübəndi sahəsindən karbohidrogen mayelərinə məruz qalmayan torpaqlarla müqayisə etmək üçün hər iki sahədən nümunələrin maqnit parametrlərini araşdırdıq. Maqnit parametrlərinin öyrənilməsi nəticəsində Pirallahı neft yatağının bəzi maqnit parametrlərinin Dübəndi bölgəsindən yüzlərlə (və ya daha çox) dəfə çox olduğu müəyyən edilmişdir. Tədqiq olunan torpaq nümunələrinin həm maqnit, həm də kimyəvi tədqiqatları maqnit minerallarının mövcudluğunu göstərdi: maqnetit və hematit. Pirallahı neft yatağı üçün maqnitləşmə daşıyıcısı maqnetitdir. Dübəndi bölgəsi üçün hematit maqnit mineraldır. Beləliklə, petromaqnit tədqiqatları və kimyəvi analizlər nəticəsində Pirallahı neft yatağı üzərində müşahidə olunan maqnit siqnalının artmasının səbəbi müəyyən edilmişdir. Pirallahı neft yatağının tədqiq edilmiş torpaqlarında aşkar edilmiş maqnetit dənələri incə dənəli maqnit fraksiyasına aiddir. Karbohidrogenlərə məruz qalmayan Dübəndi bölgəsində maqnitləşmə daşıyıcısı olaraq incə dağılmış hematit aşkar edilmişdir.

Açar sözlər: *petromaqnetizm, torpaq maqnetizmi, karbohidrogenlər, Pirallahı neft yatağı*