

Modeling the hydrothermal impact on the Jurassic deposits of the West Siberian sedimentary basin (series with H_2O and H_2O_2)

M. Yu. Zubkov

West Siberian Geological Center LLC, Tyumen, Russian Federation

E-mail: ZubkovMYu@mail.ru

Abstract. The results of hydrothermal modeling of the formation of epigenetic mineral associations and secondary reservoirs in various types of sedimentary rocks of the Jurassic age in Western Siberia in the H_2O - H_2O_2 system are considered. The experiments were carried out at a temperature of 390°C, a pressure of 70 MPa and H_2O_2 concentrations varying from 0 to 37.5%. The duration of the experiments was 10 days. In all experiments, a pyrite mixture was added as a buffer. It was found that in experiments in which there was no H_2O_2 , that is, the hydrothermal fluid consisted only of water, there was an intense formation of bitumen and volatile components from the organic matter present in the initial samples. The process of generation of bitumen and volatile components was accompanied by fluid fracturing of rocks and the formation of secondary porosity. Under these conditions, carbonates (calcite, siderite), plagioclases, and kaolinite turned out to be unstable. On the contrary, the formation of hydrothermal ferruginous chlorite was noted. Dissolution of unstable mineral phases by hydrothermal fluid led to the formation of additional secondary porosity. As the concentration of H_2O_2 and, accordingly, oxygen in the composition of the hydrothermal fluid increased, more and more complete oxidation of the organic matter present in the composition of the sediments was noted until its complete disappearance. With an increase in the oxygen concentration in the composition of the hydrothermal fluid, the appearance of first magnetite and then hematite, native sulfur, and anhydrite was observed. Under hydrothermal conditions with a maximum oxygen concentration, the formation of kaolinite and various sulfates in addition to anhydrite, represented by millosevichite, alum, as well as phases with the participation of elements that make up autoclaves, nickel and chromium sulfates, was noted. Intensive silicification of the sample surface is noted, as well as the constant presence of amorphous silica, which, along with various sulfates, is a quenching phase. These mineral phases are separated from the supersaturated hydrothermal fluid due to its rapid cooling and do not have time to form well-faceted crystals, but are present in the form of loose microporous aggregates. Along with kaolinite, the formation of hydrothermal film illite is noted.

The results obtained indicate that the presence of bitumen in the Jurassic sediments is an important exploratory feature, indicating that in this place they were subjected to hydrothermal action, which means, firstly, secondary reservoirs with high filtration and capacity properties were formed, and second, there was an intensive generation of hydrocarbons and, as a consequence, the formation of hydrocarbon deposits.

Keywords: Jurassic deposits, hydrothermal fluids, H_2O - H_2O_2 system, bitumen, fluid fracture, secondary collectors

Recommended citation: Zubkov M.Yu. (2020). Modeling the hydrothermal impact on the Jurassic deposits of the West Siberian sedimentary basin (series with H_2O and H_2O_2). *Georesursy = Georesources*, 22(4), pp. 30–40. DOI: <https://doi.org/10.18599/grs.2020.4.30-40>

Introduction

Wells drilled into the pre-Jurassic complex often reveal thick bleached zones in the overlying Jurassic sedimentary rocks (Zubkov et al., 1991; Zubkov, Vasiliev, 1991; Zubkov, 2015a; Zubkov, 2017). These bleached rocks show signs of hydrothermal alteration with characteristic mineral associations of hydrothermal origin (Zubkov et al., 1991; Zubkov, Vasiliev, 1991;

Zubkov, 2017). The bleaching process is especially pronounced in carbonaceous-clayey sediments, in which the bleaching zones gradually in the direction of the bottom-up acquire an increasingly dark color as the hydrothermal effect on these rocks weakened (Figure 1a, b) (Zubkov, Vasiliev, 1991; Zubkov, 2015a).

The bleaching of sedimentary rocks containing organic matter (OM) suggests the presence of an oxidizer, most likely oxygen, in the composition of hydrothermal fluids (HF). Indeed, the presence of oxygen in the composition of fluids separated from magmatic bodies was convincingly proved by V.I. Bgatov in his

monograph, small in volume, but rich in factual material (Bgatov, 1985).

In order to test the assumption made about the presence of oxygen in the composition of hydrothermal fluids and its participation in the transformation of the Jurassic sediments, experiments were carried out with high-temperature solutions containing various oxygen concentrations in their composition. Carbonaceous mudstones, sandstone, and gravelstone of the Lower Jurassic age were chosen as the initial samples.

Hydrogen peroxide (H_2O_2) in various ratios with water was used as an oxygen source in the hydrothermal experiments carried out.

The experiments were carried out at the Sobolev Institute of Geology and Mineralogy of the Siberian Branch of the Russian Academy of Sciences under the guidance of Doctor of Geological and Mineralogical Sciences, Professor G. Yu. Shvedenkov (Zubkov, Shvedenkov, 2002).

Apparatus and methods

The experiments were carried out in reactors (autoclaves) with a volume of about 10 cm^3 , made of stainless steel, the pressure in which was set according to the filling factor, based on the relationship between pressure, volume, and temperature in this system (Handbook of physical constants of rocks, 1969).

Samples for experiments were prepared as follows. Using a diamond saw, rectangular columns with a cross section of about 1 cm^2 and a length of about 2–3 cm were

cut out. The samples were placed in a reactor, filled with distilled water, and the required amount of H_2O_2 was added (GOST 177-88, concentration 30–40%).

In the autoclave, during its heating, hydrogen peroxide rapidly decomposed with the formation of water and oxygen:



After the experiments, the samples were examined and described under a binocular microscope, and then examined using X-ray diffraction analysis (XRD) and scanning electron microscope (SEM). The purpose of the latter procedure was to determine the changes in the structure of the pore space after hydrothermal treatment, as well as to detect newly formed minerals and their associations. Changes in mineral composition were recorded mainly on the sample surface. In addition, part of the precipitation formed during the experiments was also studied.

The experiments were carried out at a temperature of 390°C and a pressure of 70 MPa. The specified temperature value was selected in accordance with the results of determining the homogenization temperature of gas-liquid microinclusions in quartz crystals, selected by the author from the KS_1 reservoir of the Salym field. The duration of the experiments was 10 days. The oxygen concentration in the HF was set with an H_2O_2 solution. The H_2O/H_2O_2 volume ratio varied from 8/0 to 5/3. Pyrite charge was added to all autoclaves as a buffer in the amount of 1.65 g.

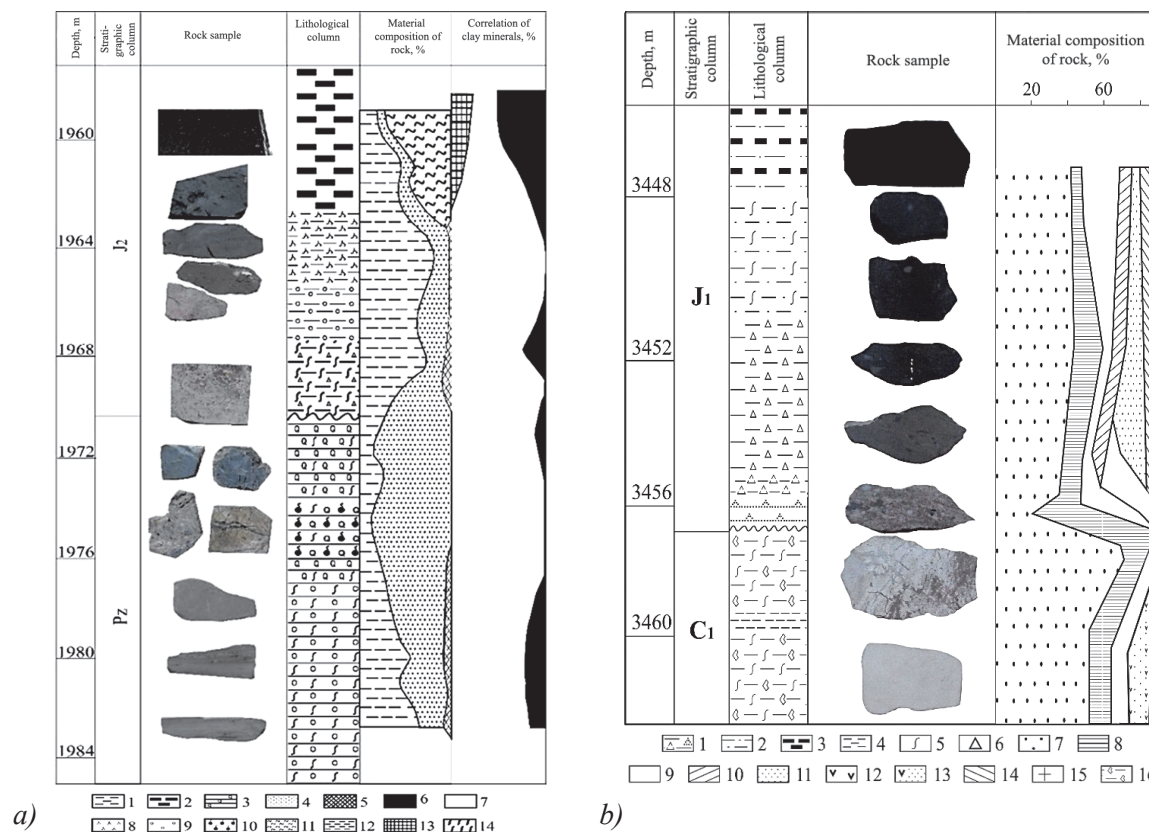


Fig. 1. Lithological sections with zones of clarification of basal Jurassic sediments and the roof of the pre-Jurassic complex along the wells of the Ubinsky (a) and Severo-Varyogonsky (b) fields (according to Zubkov, Vasiliev, 1991; Zubkov, 2015a)

The assessment of the formation of secondary porosity was carried out only at a qualitative level, since it arose mainly in the near-surface part of the sample, since the sample-hydrothermal fluid (HF) system was closed and the process of dissolution of the sample with the fluid stopped as it was saturated with dissolved mineral components. In addition, on the surface of the samples, after the completion of the experiments, the deposition of thin crusts composed of newly formed hydrothermal minerals was often observed, which prevented the analysis of structural changes that occurred on their surface and, in particular, the assessment of the value of secondary porosity. Therefore, to analyze the nature of the dissolution or leaching of the surface of the samples under the action of HF, if possible, areas were selected where there were no deposits of secondary minerals of hydrothermal origin.

In order to demonstrate the changes that occurred with the initial samples as a result of exposure to HF with different oxygen concentrations in them, the experimental results are presented in Table 1.

Research results

The first four experiments were carried out with a sample of dark gray *carbonaceous silty mudstone* with thin carbonaceous interlayers and dispersed plant detritus. It is composed mainly of kaolinite, chlorite and illite with a small content of fragments of quartz and plagioclases of fine-silt size, as well as an admixture of finely dispersed calcite.

The purpose of the experiments was to establish the regularities of changes in the mineral composition of mudstone as a result of exposure to HF, which had various oxygen concentrations in its composition, set by the ratio H_2O/H_2O_2 , which varied from 8/0 to 5/3.

After the completion of the *first* experiment with the

ratio in $HF\ H_2O / H_2O_2$ equal to 8/0, a slight lightening of the sample surface was observed, the formation of numerous droplets of bitumen on it, “melted” from the lenticules of coal. Moreover, depending on the shape of the coalified wood residues, bitumen was melted either in the form of rather isometric drops, or in the form of elongated bodies (Figure 2a-c). The pressure that arose during the transition of solid organic residues into a liquid and gaseous state exceeded the strength properties of the sample and, for this reason, fluid fracture cracks appeared in it, along which bitumen was released onto its surface (Figure 2a-c). The cavities present in the resulting bitumen droplets indicate that the process of its formation was accompanied by the release of a large amount of gaseous products, represented mainly by hydrocarbons (Figure 2b, c).

Analysis of the sample surface after the experiment showed that it underwent weak dissolution, as a result of which microvoids were formed on it, the radius of which on average does not exceed 1.2–2.5 μm (Figure 2c, d).

Comparison of X-ray diffraction data for the sample before and after hydrothermal treatment showed that the content of quartz did not change, the concentration of plagioclases slightly decreased, calcite disappeared, kaolinite completely dissolved, on the contrary, the concentration of hydrothermal chlorite increased (Table 1). Chlorite precipitated on the sample surface in the form of numerous small scale-like crystals (Figure 2d).

On the surface of pyrite grains that are part of the pyrite mixture, in some places the formation of fine-flaked hydrothermal ferruginous chlorite is also noted.

In the *second* experiment, the H_2O/H_2O_2 ratio in the HF composition was 7/1.

After the experiment, a slight bleaching of the sample surface was observed, an ochre bloom appeared, represented by small crystals of ferrous chlorite and

No.	Lithology	H_2O/H_2O_2	aSiO ₂	Anh	Hem	Ill	Qz	Kt	Ct	Mgt	Pl	Sid	Chl Ref Ht		S°	Bit
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	Carbonaceous silty mudstone	8/0	no data	+	0	>	=	<	<0	0	<	0	=	+	0	+
2	Carbonaceous silty mudstone	7/1	+	+	0	=	>	<0	<0	+	<	0	=	+	+	+
3	Carbonaceous silty mudstone	6/2	no data	+	+	=	>	<0	<0	0	<	0	=	+	+	0
4	Carbonaceous silty mudstone	5/3	+	+	+	>	>	=	<0	0	<	0	=	+	no data	0
5	Medium-grained sandstone	8/0	+	0	0	=	>	<0	0	0	<	<0	=	+	0	+
6	Medium-grained sandstone	5/3	+	+	+	=	>	=	0	0	<	<0	=	+	+	0
7	Carbonaceous mudstone	8/0	no data	0	0	>	>	<0	0	0	<	<0	=	+	0	+
8	Carbonaceous mudstone	5/3	+	+	+	=	>	=	0	0	<0	<0	=	0	+	0
9	Variegated gravelstone	5/3	no data	+	0	>	=	>	0	+	0	<0	0	0	no data	0

Table 1. The results of determining the mineral composition of various types of Jurassic rocks after exposure to hydrothermal fluids with different H_2O/H_2O_2 ratios at a temperature of 390°C and a pressure of 70 MPa. Notes: “Ref” – the original mineral phase, which is part of the Jurassic deposits; “Ht” – newly formed mineral phase of hydrothermal origin; “<” – decrease in the relative content of the mineral phase; “>” – an increase in the relative content of the mineral phase; “+” – the emergence of a new mineral phase of hydrothermal origin; “0” – no mineral phase; “=” – preservation of the original mineral phase; “<0” – decrease in content until it disappears completely; “n/a” – no data; aSiO₂ – amorphous silica; Anh – anhydrite; Bit – bitumen; Hem – hematite; Ill – illite; Qz – quartz; Kt – kaolinite; Ct – calcite; Mgt – magnetite; Pl – plagioclase; Sid – siderite; Chl – chlorite; S° – native sulfur

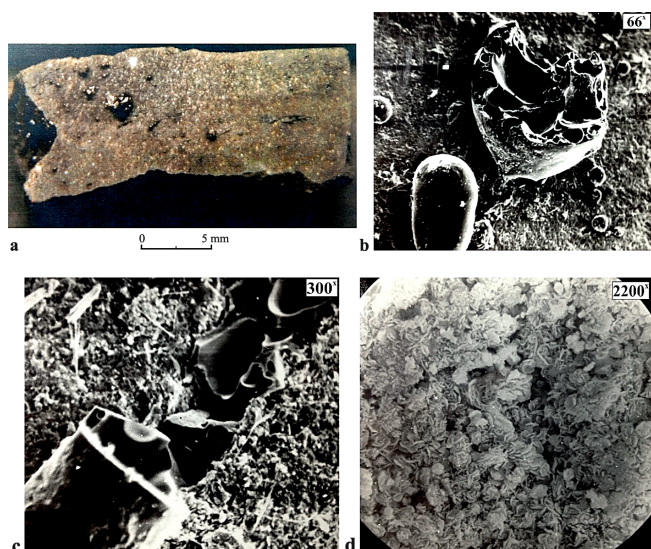


Fig. 2. Photo of a sample of carbonaceous-silty mudstone (a) and SEM images of its surface (b-d) after exposure to HF, which had an H_2O/H_2O_2 ratio of 8/0. a – the appearance of the sample after the completion of the experiment; b – drops of bitumen of various shapes and sizes; c – fluid fracture filled with formed bitumen with voids from volatiles released from it; d – enlarged fragment of its surface with numerous small scale-like crystals of hydrothermal ferruginous chlorite

magnetite (Figure 3a). Just as in the previous experiment, bitumen droplets appeared on the surface of the sample under consideration after the completion of the experiment, but their number and size are noticeably smaller than in the previous experiment (Figures 2a, 3a).

After the experiment, the surface of the sample showed signs of poor dissolution; there are thin fractures of fluid fracture, along which bitumen flowed onto it (Figure 3a, b). Judging by the elemental spectrum obtained from the sample surface, it is composed mainly of quartz, illite, and hydrothermal magnetite, as well as ferruginous chlorite (Figure 3b, left spectrum). Analysis of the elemental composition of the formed bitumen droplets showed that they have a high sulfur content, that is, this is thiobitumen (Figure 3b, right spectrum).

Comparing the results of X-ray diffraction analysis of the sample before and after exposure to HF, it can be noted that calcite and kaolinite disappeared from its surface, the plagioclase content decreased, and the chlorite content, on the contrary, increased (Table 1).

In the lower part of the sample, at the boundary with the pyrite charge, along with finely dispersed magnetite, the presence of small crystals of native sulfur is noted.

In the *third* experiment, the ratio of H_2O to H_2O_2 in the HF was 6/2.

Analysis of the sample taken out of the autoclave after the experiment showed that its surface was intensely leached, which led to the formation of numerous microvoids. In addition, due to a thin film of finely dispersed iron oxides deposited on its surface, the sample acquired a light brown color (Figure 3c). The oxygen

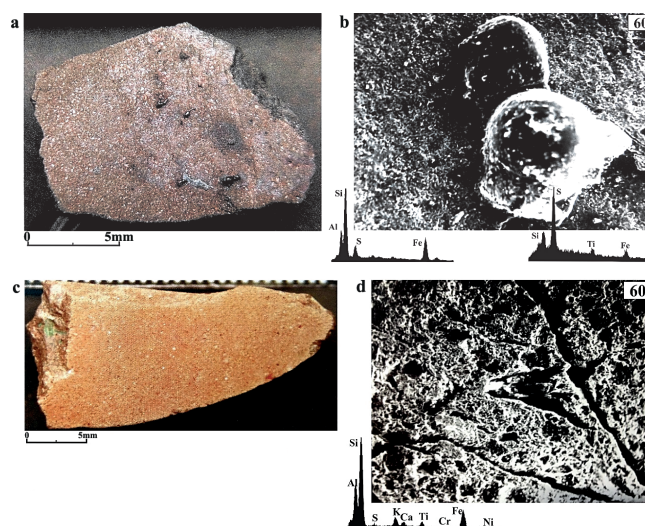


Fig. 3. Photos of samples of carbonaceous-silty mudstone (a, c) and SEM images of their surface (b, d) after exposure to HF, which had an H_2O/H_2O_2 ratio of 7/1 (a, b) and 6/2 (c, d). a – the appearance of the sample after completion of the experiment; b – bitumen drops, the elemental spectrum of which is shown to the right of the image; c – the appearance of the sample after the end of the experiment; d – microcavities on its surface, formed as a result of leaching of HF of unstable minerals and oxidation of OM and bitumen (hereinafter, under the images, the elemental spectra obtained from their area are given, unless otherwise indicated)

present in the HF oxidized the OM; therefore, under the light brown film of iron oxides, the sample surface has a light gray color.

Even at low magnification, the fractured-microporous structure of the sample surface is clearly visible, which was formed at first due to fluid fracture caused by the generation of bitumen, and then its oxidation (Figure 3d). The crack opening is 30–80 microns, and their length is more than 0.8–1.8 mm. According to the data of elemental analysis of the sample surface, it contains mainly quartz, illite, and hydrothermal minerals, represented by hematite with a small admixture of anhydrite and chlorite (Figure 3d).

Comparison of X-ray diffraction data for the sample before and after exposure to HF showed that kaolinite and calcite disappeared from its surface, the content of plagioclases decreased, on the contrary, the concentration of chlorite increased slightly, and fine-flaked hematite appeared (Table 1).

Thus, an increase in the proportion of H_2O_2 (and, accordingly, oxygen) in the composition of HF leads to the fact that the OM in the composition of the near-surface part of the sample is completely oxidized, which, in turn, causes the formation of an additional secondary capacity. In addition, due to the oxidation of OM, carbon dioxide appears in the composition of the fluid, which promotes the dissolution of minerals unstable in this thermodynamic environment, due to which an additional secondary capacity is also formed. In addition, H_2SO_4

is formed, due to the reaction of which with calcite and anorthite end of plagioclases, anhydrite appears.

In the *fourth* experiment, the ratio of water to H_2O_2 in HF was 5/3. That is, in the considered experiment, the oxygen concentration in the composition of the HF was maximum.

The sample taken from the autoclave after the experiment had a dark brown color. In its lower part, there is a linear sub-horizontal two-phase boundary (liquid-gas), indicated by small crystals of dark gray hematite (Figure 4a).

The surface of the initial sample was initially clearly lightened due to the oxidation of OM contained in it; it contains numerous fluid fractures and cavities remaining from oxidized carbonaceous residues and bitumen melted out of them (Figure 4b). The openness of the formed microcracks is 15–75 μm , and their length often exceeds 1.5–2 mm (Figure 4b).

Judging by the elemental spectrum obtained from the sample surface, it contains quartz, anhydrite, and hematite (Figure 4b). At high magnification, crystals of hydrothermal anhydrite are clearly visible, on the surface of which and near them there are numerous microcrystalline aggregates of hematite (Figure 4c with the elemental spectrum of hematite grains).

In addition to anhydrite and hematite, the surface of the sample contains felt-like aggregates of Al, K, and Na

sulfates of the alum type, as well as aluminum sulfate naturally occurring under the name millosevichite, which are probably the quenching phase that precipitated from the supersaturated HF upon cooling.

At the two-phase boundary, a flaky fine-crystalline hematite was deposited, individual crystals of which are 5–30 microns in size, along with which much larger crystals of anhydrite are present (Figure 4d). Of the original minerals that make up the sample, only quartz was preserved on its surface.

An analysis of the XRD results of the sample before and after exposure to HF with the highest oxygen content in it showed that the organic matter that was part of its composition was completely oxidized on its surface. The content of plagioclases decreased, calcite completely disappeared, the proportion of quartz increased, anhydrite, hematite, chlorite appeared, and what is very important, unlike previous experiments, kaolinite was preserved (Table 1).

In the next two experiments, a light gray medium-grained sandstone with quite numerous inclusions of charred plant detritus was used as the initial sample. It is composed mainly of detrital grains of quartz and plagioclase, clay cement is represented by kaolinite, chlorite, and illite, and carbonates are exclusively siderite microspherulites.

In the *first* experiment, the $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ ratio in the fluid was 8/0.

After the experiment, the sample surface became loose and acquired a lighter tone (Figure 5a).

Microscopic studies showed that small pores were formed on the surface of the sample due to the dissolution of unstable mineral phases, and the carbonaceous detritus present in its composition turned into bitumen, which has numerous small cavities that arose as a result of the release of gaseous products from it (Figure 5b). Judging by the elemental composition of the area under consideration, the sample surface is composed mainly of quartz with an admixture of illite (Figure 5b).

At high magnifications, the morphology of the formed microvoids, ranging in size from 3 to 20 microns, is clearly visible, as well as numerous scale-like crystals of hydrothermal chlorite (Figure 5c). Detrital quartz grains do not bear traces of changes; on the contrary, plagioclase grains were partially dissolved.

Comparison of the XRD results of the sample before and after hydrothermal treatment showed that an increase in the proportion of quartz, a decrease in the content of plagioclases, and the disappearance of kaolinite and siderite are noted on its surface. On the contrary, the concentration of chlorite increased. The illite content remained practically unchanged (Table 1).

In the *second* experiment, the ratio of $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ in HF was 5/3.

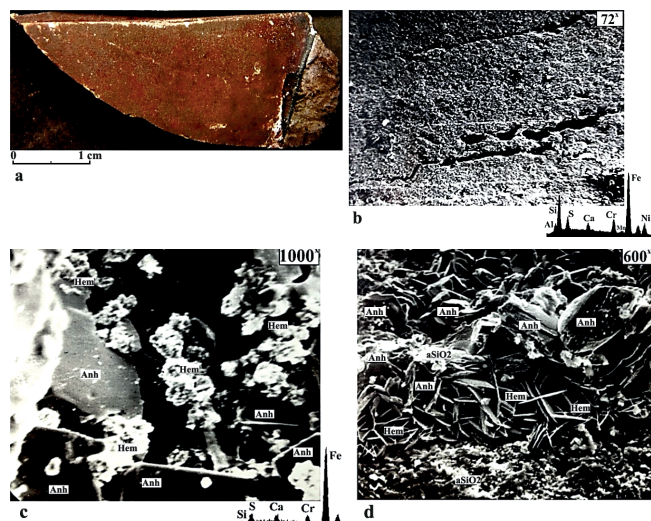


Fig. 4. Photo of a sample of carbonaceous-silty mudstone (a) and SEM images of its surface (b-d) after exposure to HF, which had an $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ ratio of 5/3. a – the appearance of the sample after the completion of the experiment; b – microcavities on its surface, formed as a result of leaching of unstable minerals HF and oxidation of the formed bitumen; c – enlarged fragment of the same area with large crystals of anhydrite (Anh) and numerous small aggregates of hematite (Hem), the elemental spectrum of which is shown below the photograph; d – numerous small lamellar crystals of Hem located at a two-phase boundary (liquid-gas), in places covered with flocculent aggregates of amorphous silica (aSiO_2)

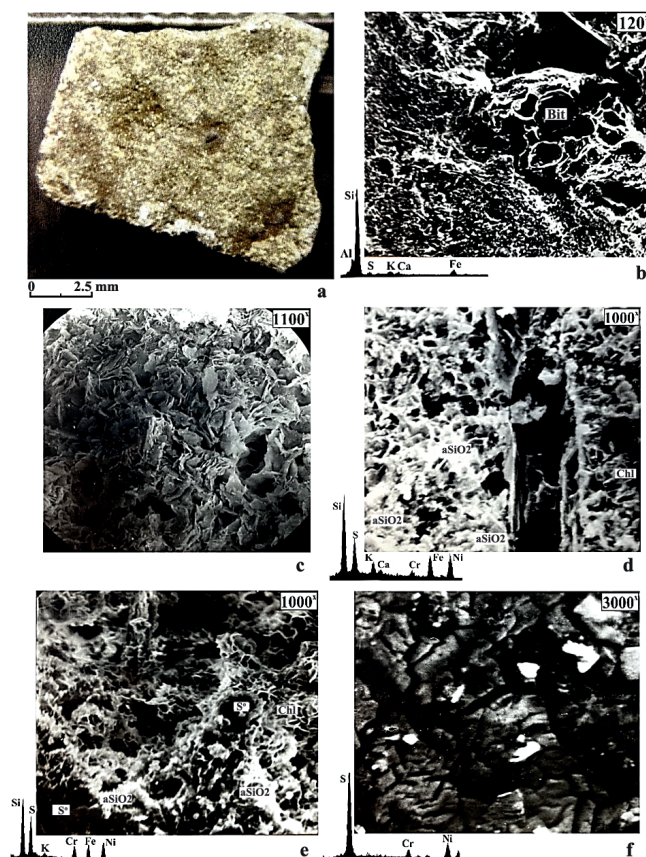


Fig. 5. Photograph of a sandstone sample (a) and SEM images of its surface (b, c) after exposure to HF having an H_2O/H_2O_2 ratio of 8/0, an SEM image of the surface of the same sandstone after exposure to it with a HF having an H_2O/H_2O_2 ratio equal to 5/3 (g) and SEM images of the precipitate formed in the autoclave after this experiment (e, f). a – the appearance of the sample after the completion of the experiment; b – bitumen (Bit) with microcavities from gaseous products released from it; c – enlarged fragment of the sample surface with numerous scale-like microcrystals of illite and hydrothermal chlorite; d – a cavity left over from oxidized carbonaceous detritus, surrounded by a fibrous mass of sulfates, as well as $aSiO_2$ with an admixture of small crystals of Chl, Hem and Anh; e – the surface of a crust composed of native sulfur (S_0) and a felt-like mass consisting of sulfates, Chl, Hem and $aSiO_2$; f – an enlarged fragment of the same crust, shot in the COMPO mode: the dark gray mass is S_0 , the elemental spectrum of which is shown next to the image

After the experiment, the appearance of two regions on the surface of the sample: brown and light gray, almost white, separated by an even rectilinear boundary separating the two-phase region (gas-liquid).

The surface of the sample bears traces of intense leaching. In addition, thin crusts of newly formed phases are noted on it, of which a brown bloom, represented by microcrystalline hematite, is best distinguished. Interestingly, newly formed anhydrite aggregates often lie directly on leached plagioclase grains, which unambiguously indicates that the calcium necessary for the formation of anhydrite was extracted from them.

On the leached sandstone surface, there are thin films and flakes of newly formed phases, represented, judging by the results of elemental analysis, mainly by silica, iron oxides, and also sulfates. As a result of the interaction of the sample with HF, its surface was silicified (Figure 5d).

An analysis of the XRD results of the sample before and after exposure to HF with a high initial oxygen concentration in it showed that after the experiment, plagioclase and siderite almost completely disappeared from its surface, on the contrary, the proportion of chlorite and kaolinite increased, anhydrite and hematite, as well as Ni and Cr sulfates appeared (Table 1).

The sediment raised from the bottom of the autoclave after the experiment was very loose microporous microgranular and felt-like aggregates with a close set of their constituent elements to that which was obtained from the surface of the sample itself (Figure 5e). Judging by their elemental composition, they contain a lot of amorphous silica and various sulfates, possibly oxides, as well as native sulfur (Figure 5f).

In contrast to the previous experiment, in which there was no H_2O_2 in the composition of HF and the decomposition of kaolinite with the formation of hydrothermal chlorite was observed, in the experiment under consideration, along with chlorite, kaolinite is also present (Table 1).

In the next two experiments, a thin-layered carbonaceous mudstone, composed mainly of kaolinite, chlorite, illite, and detrital grains of quartz and plagioclases of fine-aleurite dimension, and also containing a small admixture of small concretions of siderite, was used as an initial sample.

In the first experiment, the ratio of H_2O to H_2O_2 in HF was 8/0. After the experiment, a barely noticeable lightening of the sample surface was noted, as well as traces of its weak leaching, in addition, small rare droplets of bitumen formed from carbonaceous detritus appeared on it (Figure 6a).

Microscopic analysis showed that bitumen melted and flowed out to the surface along fluid fractures, and instead of the carbonaceous layers themselves, open cavities appeared, the opening of which is 10-30 microns (Figure 6b, c).

In addition to fluid fractures and cavities, round-shaped microcaverns (10–50 μm in diameter) are noted, most likely due to the dissolution of the HF siderite microbundles (Figure 6b).

Judging by the results of the elemental analysis of the sample surface after the experiment, it is composed mainly of quartz, illite, and chlorite (Figure 6c). Small grains of light gray (almost white) color pyrite, deposited mainly on the surface of bitumen, which has a dark gray (almost black) color in the image, are clearly visible in the photograph of the same area of the sample, made in COMPO mode (Figure 6d).

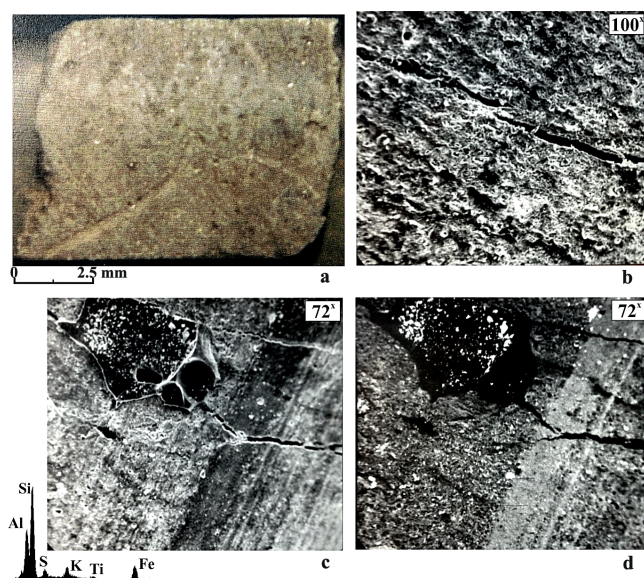


Fig. 6. Photo of a sample of carbonaceous mudstone (a) and SEM images of its surface (b-d) after exposure to HF, which had an H_2O/H_2O_2 ratio of 8/0. a – general view of the sample after the experiment; b – leached surface with fluid fractures; c – a split bitumen drops formed from carbonaceous detritus surrounded by fluid fractures; d – the same area taken for comparison in the COMPO mode, light microparticles – pyrite

The results of X-ray diffraction analysis of the sample surface obtained before and after hydrothermal treatment showed that the action of HF caused a sharp decrease in the content of plagioclases, siderite and kaolinite completely dissolved. On the contrary, the content of hydrothermal chlorite increased. No noticeable changes in the concentration of illite are observed, but the content of quartz clearly increased, and the surface of the sample was silicified (Table 1).

In the *second* experiment, in the composition of HF, the H_2O/H_2O_2 ratio was 5/3. After the completion of the experiment, the surface of the sample acquired a light gray color, however, iron oxides were deposited on the sample (especially in its lower part), giving it a dark gray, sometimes with a brownish tint (Figure 7a). Intensive dissolution of unstable minerals and oxidation of OM, which was part of the carbonaceous mudstone, are noted.

Analysis of areas covered with a dark gray film with a brownish tint showed that they are composed of several mineral phases. In order to isolate minerals composed of heavier elements, the same area was surveyed in normal and COMPO modes (Figure 7c, d, respectively). The image taken in the COMPO mode clearly shows hematite grains, which have a light gray color (Figure 7d). Almost in the central part of the images, there is a large aggregate of native sulfur (about 0.1 mm in diameter), which has a dark gray, almost black color (Figure 7d with the elemental spectrum of sulfur).

Comparison of the results of X-ray structural analysis of the sample surface, obtained before and after its hydrothermal treatment, showed that the action of HF led

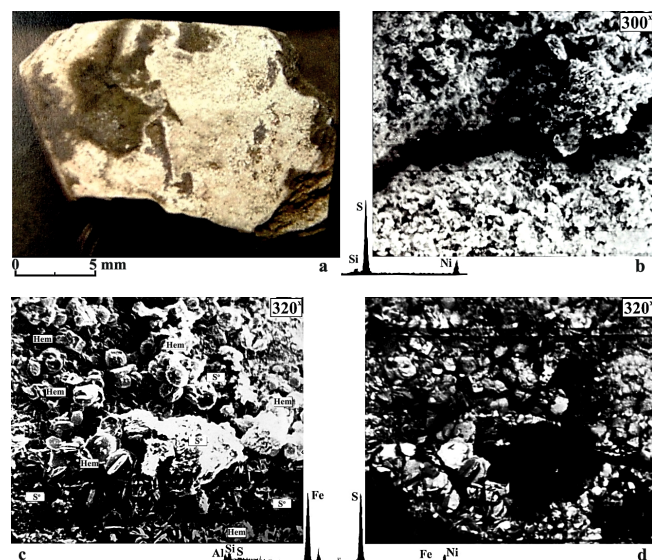


Fig. 7. Photo of a sample of carbonaceous mudstone (a) and SEM images of its surface (b-d) after exposure to HF, which had an H_2O/H_2O_2 ratio of 5/3. a – general view of the sample after the experiment; b – microcrack formed as a result of fluid fracture and subsequent oxidation of the bitumen (Bit) present in it, surrounded by small aggregates of S_0 and Ni sulfate; c – an area with numerous small aggregates of lamellar crystals of Hem, the elemental spectrum of which is shown below the photograph; d – the same area, shot for comparison in the COMPO mode, on which a large S_0 grain is located almost in its center, the elemental spectrum of which is shown under the image (light particles – Hem, dark to almost black areas are built by S_0)

to almost complete dissolution of plagioclase and siderite. The chlorite concentration slightly decreased, kaolinite remained, and their crystal structure is characterized by weak ordering (the peaks in the diffractograms became broader, and their intensity decreased). The proportion of quartz has significantly increased. Hematite, anhydrite, native sulfur, and Ni sulfate appeared (Table 1). The OM, which was present in the near-surface part of the sample and the bitumen formed from it, completely oxidized, which led to the formation of additional porosity in the initial sample.

In the last experiment, “*variegated*” gravelstone composed of quartz fragments cemented by kaolinite and illite with a small admixture of small siderite oolites was subjected to hydrothermal action (Figure 8a). This sample was taken from the YK_{11} basal layer of the Talinskaya area and, in contrast to those considered earlier, was subjected to hydrothermal action in natural conditions (Zubkov et al., 1991; Zubkov, 2017). The ratio of H_2O and H_2O_2 in HF in the considered experiment was 5/3.

After the experiment, three zones were formed on the surface of the sample. The lower zone, bordering with the pyrite mixture, slightly changed the original color, the middle one acquired a brown hue, and the upper one turned out to be intensely lightened (Figure 8b). Most likely, there were two phases in the autoclave – the lower

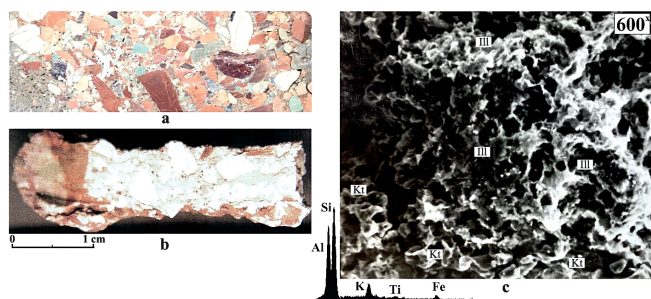


Fig. 8. Photos of the initial sample of “variegated” gravelite (a) and the same sample after the experiment (b), and SEM image of the surface of the latter after exposure to HF (c), which had an H_2O/H_2O_2 ratio of 5/3. a – general view of the original sample; b – same after the experiment; c – a fragment of its surface, which contains poorly crystallized aggregates of kaolinite (Kt) (bottom) and film of illite (Il) (the rest of the porous mass)

part of the autoclave was filled with liquid, and the upper part was filled with gaseous phases.

Analysis of the composition of the newly formed phases showed that the brown deposit on the sample surface is represented by magnetite. The near-surface part of the leached grains turned out to be covered with poorly crystallized kaolinite with film illite (Figure 8c). Rare small siderite oolites that were present on the surface of the sample dissolved as a result of interaction with HF, and thin crusts of magnetite were formed in their place, lining the surfaces of voids that remained in place of these oolites (Figure 8b).

It should be noted that as a result of the hydrothermal treatment of the “variegated” gravelite, in contrast to the previously considered experiments, minimal changes were observed in its mineral composition and structure of its surface. Chlorite was not formed in this experiment (Table 1).

Discussion of the results

Despite the different lithological composition of the samples participating in the experiments, similar patterns were observed in the changes in their mineral composition and in the formation of mineral phases of hydrothermal origin, depending on the oxygen content in the HF (Table 2).

In experiments in which the HF consisted only of water, the dissolution of plagioclases, carbonates, pyrite, and kaolinite was observed, and the initial OM was transformed into thiobitumen and volatile components, and this process was accompanied by fluid fracture. All these hydrothermal transformations of the samples led to the formation of secondary porosity in them (Figures 2b, c, 5c, 6b).

The newly formed phases in the considered experiments are represented by bitumen, hydrocarbon volatiles, chlorite, anhydrite, and amorphous silica (Figures 2b-d, 5b, c, 6c, d).

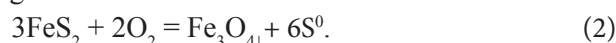
Hydrothermal chlorite was formed due to the dissolution of kaolinite, plagioclase and siderite, as well as partly of the pyrite mixture. Al and Si came from the first two minerals, and Fe from the last two.

A small amount of anhydrite arose as a result of the oxidation of pyrite sulfur and/or sulfur in the composition of thiobitumens with the presence of atmospheric oxygen in the autoclave, with the formation of a sulfate ion, and the source of Ca was the dissolved by HF calcite and the anorthite end of plagioclases.

Amorphous silica was a quenching phase that was dissolved in the composition of the HF and precipitated from it as a result of rapid cooling (quenching) of the autoclaves. Under natural conditions, silica dissolved in HF is released in the pore space of sandstones in the form of regeneration faces of detrital quartz grains and/or in the form of its small crystals (Zubkov et al., 1991; Zubkov, 2017).

In addition to bitumen, as a result of the hydrothermal impact on the original OM of the Jurassic sediments, a large amount of volatile components are formed, which include hydrocarbons from C_1 to, probably, C_{25} , if we take into account the HF temperature of 390°C. The high content of sulfur in the bitumen probably indicates that the hydrocarbons released as a result of hydrothermal pyrolysis from the initial OM practically do not contain heteroatoms that accumulate in the “residual” product, thiobitumen.

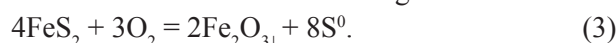
The appearance of a noticeable amount of oxygen in the HF composition ($H_2O/H_2O_2 = 7/1$) led to almost complete oxidation of the initial OM (Figure 3a) and the formation of new hydrothermal phases, represented by magnetite and native sulfur:



The formation of anhydrite is explained by the oxidation of pyrite and/or sulfur with oxygen to sulfuric acid and its interaction with Ca, which enters the HF as a result of the dissolution of calcite and plagioclase grains.

Similar to the experiments in which HF was absent from H_2O_2 , the experiment under consideration shows the formation of hydrothermal chlorite and amorphous silica, as well as dissolution of calcite, siderite, plagioclase, and kaolinite (Table 2).

A further increase in the oxygen concentration in the composition of HF ($H_2O/H_2O_2 = 6/2$) leads to the complete oxidation of OM and bitumen, as well as the formation of hematite instead of magnetite:



Moreover, in addition to hematite, a large amount of native sulfur is formed (equation (3)). Oxidation of OM and the bitumen formed from it assumes the following reaction in the autoclave:



Consequently, in the composition of HF as a result of the reactions of O_2 with OM in the autoclave, CO_2 will appear.

	H ₂ O/H ₂ O ₂ ratio			
	8/0	7/1	6/2	5/3
Hydrothermal neocrystallisation	Bitumen, Chlorite, Anhydrite, Amorphous silica	Bitumen, Chlorite, Anhydrite, Amorphous silica, Magnetite, Native sulfur	Chlorite, Anhydrite, Hematite, Amorphous silica, Native sulfur	Chlorite, Kaolinite, Illite, Hematite, Anhydrite, Amorphous silica, Native sulfur
Increase in the relative content of quartz				
Unstable phases	Kaolinite, Calcite, Initial OM, Plagioclase, Siderite, Pyrite	Calcite, Kaolinite, Plagioclase, Initial OM, Siderite, Pyrite	Calcite, Kaolinite, Plagioclase, Initial OM, Siderite, Pyrite	Calcite, Plagioclase, Initial OM, Siderite, Pyrite

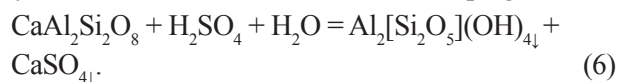
Table 2. Results of determining the mineral composition of various types of Jurassic rocks after exposure to hydrothermal fluids with different H₂O/H₂O₂ ratios at a temperature of 390°C and a pressure of 70 MPa

An even greater increase in the oxygen concentration in the HF composition (H₂O/H₂O₂ = 5/3) causes the same changes in the composition of the samples as in the experiments with its lower concentration. The only important difference between these experiments from the previous ones is the preservation or, possibly, the formation of hydrothermal kaolinite (Table 2).

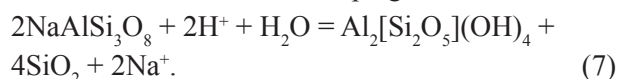
Most likely, this fact is explained by the very high acidity of HF due to the formation of a large amount of sulfuric acid as a result of the oxidation of pyrite and sulfur:



Under these conditions, the formation of kaolinite and anhydrite occurs due to the anorthite end of plagioclases:



The kaolinitization process in an acidic medium can also be demonstrated by the example of the reaction of acidic HF with the albite end of plagioclases:



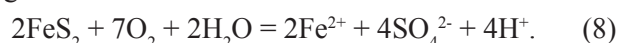
It follows from the above equation that as a result of the formation of hydrothermal kaolinite in an acidic medium, silica is necessarily formed, that is, the initial samples are silicified.

Thus, under the action of HF with a high oxygen content, intense silicification of the sample surface occurs, which is associated with the formation of a large amount of sulfuric acid and, accordingly, high acidity of HF. Under these extremely acidic conditions, almost all elements are dissolved and carried out except for silica, which has an extremely low solubility in acidic HF (Borisov, 2000; Garrels, Christ, 1968; Zubkov, 2015a; Zubkov, 2017; Naboko, 1962; Smirnov, 1982; Sokolov, 1971).

Experiments have shown that chlorite is a higher-temperature phase than kaolinite. However, under very acidic conditions, even at high temperatures (390°C), both minerals occur together (Table 2). It is possible that

chlorite is a metastable phase under these conditions. This is also evidenced by the fact that in the experiment with “variegated “ gravelite at the maximum oxygen content in the HF (H₂O/H₂O₂ = 5/3), the formation of hydrothermal chlorite was not observed, but kaolinite was retained (Tables 1, 2).

It is possible that the formation of ferrous chlorite is provoked by the presence of a pyrite mixture, which, when interacting with an oxygen-containing hydrothermal fluid, dissolves with the formation of a large number of iron ions and sulfuric acid:



It was found that in all the experiments with the participation of HF, unstable phases were calcite, siderite, pyrite, plagioclase, OM, and kaolinite (except for experiments with a high concentration of the formed sulfuric acid).

The dissolution of these mineral phases and the transformation of OM into bitumen leads to the formation of secondary porosity. Consequently, the areas within which the GOR was introduced into the Jurassic deposits should be characterized by increased filtration and storage properties. In addition, high-temperature HF actively affect the initial organic matter present in the Jurassic sediments, causing the active generation of hydrocarbons, which, having dissolved in themselves some of the resinous-asphaltene components that make up the bitumen, migrate into the reservoir rocks. The remaining bitumen, consisting of the highest molecular weight hydrocarbons and hetero-compounds, due to its low mobility (due to high viscosity), remains in place or migrates a short distance from the parent rocks.

The most striking example of the above-described model of hydrocarbon and bitumen generation under the influence of HF is the Bazhenov formation. In areas where its sediments were exposed to high-enthalpy HF on the surfaces of cracks and/or caverns, there are various minerals of hydrothermal origin, represented, for example, crystals of quartz, magnesian calcite, barytocalcite, and

others, surrounded and partially covered with bitumen formed from the initial organic matter included in its composition (Figure 9a-c). There are often thin lenticles of bitumen, also formed as a result of hydropyrolysis of the initial OM of the Bazhenov Formation by a hydrothermal fluid (Figure 9d). Therefore, the classics were right when they called the deposits of the Bazhenov Formation bituminous, at least in those areas where they were subjected to hydrothermal action.

Bitumen is also found in the pore space of the so-called pseudoquartzites, composed of small crystals of hydrothermal quartz (layer Y_1^0), found within the Gribnoye and Akhtamarskoye deposits (Figure 10a-d). Most likely, under the action of HF, bitumen was formed from the OM of the Bazhenov formation, overlying this layer, and penetrated into the pore space of pseudoquartzites, due to the high temperature, having sufficient plasticity and, accordingly, mobility.

In the pore space of the Jurassic sandstones on the Krasnoleninsky arch and in the Shaimsky petroleum province also bitumen is found (Figure 10e, f). Most often, these sandstones are located at a short distance from the oil and gas source deposits, which were also exposed to high-enthalpy HF. In the areas under consideration, these are analogs of the Bazhenov formation (Lower Tutleim and Lower Danilov sub-formations).

Thus, the detection of bitumen in the Jurassic sediments is an important exploratory feature, indicating that in this place there was an impact of HF on the oil source rocks, which, as a result of this impact, actively generated hydrocarbons, and additional (secondary) porosity was formed in the reservoir rocks.

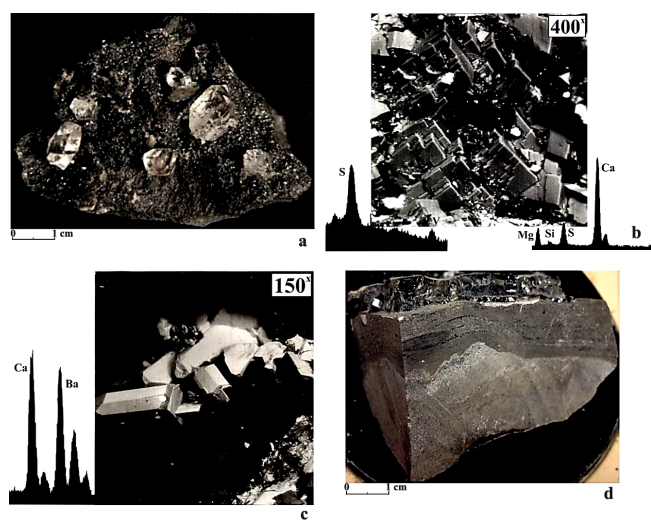


Fig. 9. Bitumen in the Bazhenov formation: Em-Egovskaya (a), Palyanovskaya (d) areas and Maslikhovskoe (b, c) oil field. Crystals of hydrothermal minerals surrounded and partially covered with bitumen: a – quartz; b – magnesian calcite, the elemental spectrum of which is located on the right, and on the left – the spectrum of vanadium-bearing thiobitumene; c – barytocalcite and its elemental spectrum; d – lenticle of thiobitumene

In conclusion, we note that the study of the mineral composition of the samples taken from the bleached Jurassic deposits showed that they lack magnetite and, moreover, hematite of hydrothermal origin (Zubkov et al., 1991; Zubkov, 2017). Nevertheless, the organic matter present in their composition turned out to be completely or almost completely oxidized.

They contain hydrothermal minerals: sulfates (anhydrite, barite), kaolinite, siderite, quartz, and, in rare cases, native sulfur (Zubkov et al., 1991; Zubkov, 2015b; Zubkov, 2017). From these facts, it can be concluded that the oxygen concentration in natural HF was much lower than in the experiments performed. But since the volumes and time of the impact of natural HF on the initial

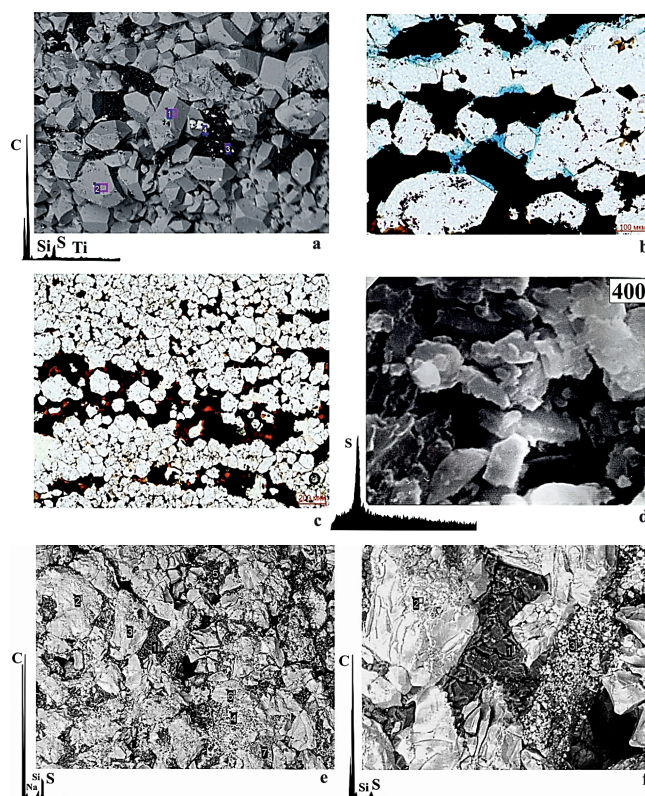


Fig. 10. Bitumen in pseudoquartzites (layer J_{10}) of the Gribnoye (a, b) and Akhtamarskoye (c, d) deposits, as well as in sandstone (layer P_1) of the Shaimsky petroleum province (e, f). a – SEM image of numerous crystals of hydrothermal quartz, the pore space between which is filled with thiobitumen, the elemental spectrum of which is located under the image; b – transparent petrographic thin section of the same sample, stained with blue resin, in which the pore space is almost completely filled with thiobitumen; c – a transparent petrographic thin section, stained with red resin, in which it is also seen that almost all the pore space between quartz crystals is filled with thiobitumen; d – enlarged fragment of the SEM image of the same sample, which contains a lumpy thiobitumen aggregate, the elemental spectrum of which is shown below the image; e – SEM image of sandstone, the pore space in which is occupied by thiobitumen, the elemental spectrum of which is shown below the image; f – enlarged fragment of the previous image with thiobitumen and its elemental spectrum

Jurassic sediments were much more significant than in the performed experiments, the OM in their composition, despite the low concentration of oxygen in the HF composition, had time to oxidize. In addition, one should not forget that in the experiments carried out, the system was closed and the products of hydrothermal reactions accumulated in autoclaves, while natural systems, as a rule, are open to certain degree, and the resulting products have the ability to leave the place where they formed.

Intensive decomposition of carbonates in the performed experiments is explained by the absence of carbonate ions in the composition of the HF, which had a purely aqueous composition. In experiments in which H_2O_2 was present, an acidic environment arose in the additives due to the formation of sulfuric acid; therefore, carbonates were easily dissolved in acidic HF. Consequently, natural hydrothermal fluids contained much less oxygen in their composition than in the experiments performed, and in addition, they contained a sufficient amount of carbonate ions necessary for the formation of carbonates and, first of all, having an iron composition.

OM, which was part of the Jurassic sediments, acted as a buffer, which contributed to the preservation of the bivalent state of Fe contained in the HF. Due to this, siderite and ankerite are often present in the clarified Jurassic sediments, along with hydrothermal quartz and kaolinite (Zubkov et al., 1991; Zubkov, 2017). The absence of hydrothermal chlorite in the Jurassic sediments exposed to HF also indicates that they had an acidic composition and, probably, a lower temperature than in the experiments carried out.

Conclusions

1. In experiments with HF having a purely aqueous composition, an intensive generation of hydrocarbons and bitumen from the initial OM is observed, which is accompanied by fluid fracture of the rock and leads to the formation of additional secondary porosity.

2. In the same experiments, dissolution of unstable minerals occurs, as a result of which secondary porosity is also formed, the filtration-capacitive properties of rocks are improved and their silicification occurs.

3. As the share of H_2O_2 in the composition of HF increases, the primary oxidation of the initial OM and bitumen formed from it is observed, the decomposition of carbonates, kaolinite and plagioclases, the appearance of magnetite first, which then, as the concentration of H_2O_2 (oxygen) increases, is replaced by hematite, native sulfur and anhydrite are formed and ferrous chlorite.

4. In experiments with the maximum concentration of H_2O_2 and, accordingly, high acidity of the hydrothermal fluid, kaolinite is preserved.

5. The results obtained indicate that natural hydrothermal fluids had a lower oxygen concentration in their composition than in the experiments performed, since iron oxides were not found in the areas exposed to

them, although Ca and Ba sulfates, native sulfur were present, and the rocks are intensely lightened.

6. The presence of siderite and kaolinite in rocks subjected to hydrothermal action under natural conditions, but the absence of chlorite in them indicates that natural hydrothermal fluids probably had a lower temperature (less than 390°C), acidic composition and were saturated with carbonate ion, which was absent or was present in an insignificant amount in the composition of hydrothermal fluid in the experiments performed.

7. The discovery of bitumen in the Jurassic sediments of the West Siberian (and other) sedimentary basins is an important exploratory indicator that in this area the rocks were subjected to hydrothermal action, which caused the active generation of hydrocarbons from the original OM and the formation of secondary porosity, which together with a high probability could lead to the formation of hydrocarbon deposits with high filtration and reservoir properties.

References

- Bgatov V.I. (1985). The history of oxygen in the Earth's atmosphere. Moscow: Nedra, 87 p. (In Russ.)
- Borisov M.V. (2000). Geochemical and thermodynamic models of vein hydrothermal ore formation. Moscow: Nauchnyi Mir, 360 p. (In Russ.) <https://doi.org/10.1023/A:1002865109271>
- Handbook of Physical Constants. (1969). Clarke, S.P., Jr., Ed. Trans. under the title Spravochnik fizicheskikh konstant gornykh porod. Moscow: Mir, 1969. (In Russ.)
- Garrels R.M., Christ C.L. (1968). Solutions, minerals, equilibria. Moscow: Mir, 318 p. (In Russ.)
- Naboko S.I. (1962). Formation of modern hydrothermal fluids and metamorphism of solutions and rocks. *Volcanism issues*, pp. 52–62. (In Russ.)
- Smirnov V.I. (1982). Geology of minerals. Moscow: Nedra, 670 p. (In Russ.)
- Sokolov V.A. (1971). Geochemistry of natural gases. Moscow: Nedra, 336 p. (In Russ.)
- Zubkov M.Yu. (2015a). Secondary reservoirs of tectonic-hydrothermal origin in the roof of the pre-Jurassic complex in the West-Siberian plate and its forecast methods. *Geologiya nefi i gaza = Russian Oil and Gas Geology*, 6, pp. 78–95. (In Russ.)
- Zubkov M.Yu. (2015b). Peculiarities of uranium distribution in bituminous deposits of the Bazhenov formation (Western Siberia). *Karotazhnik*, 5(251), pp. 3–32. (In Russ.)
- Zubkov M.Yu. (2017). Tectonic-hydrothermal processes in the West Siberian Jurassic deposits. *Geologiya nefi i gaza = Russian Oil and Gas Geology*, 1, p. 60–76. (In Russ.)
- Zubkov M.Yu., Dvorak S.V., Romanov E.A., Chukhlantseva V.Ya. (1991). Hydrothermal processes in the Sherkala member of the Talinskoye field (Western Siberia). *Lithology and Mineral Resources*, 3, pp. 122–132. (In Russ.)
- Zubkov M.Yu., Shvedenkov G.Yu. (2002). Experimental modeling of the formation of secondary reservoirs under the influence of hydrothermal fluids of various compositions. *V Sci. and Pract. Conf.: Ways of realizing the oil and gas potential of the Khanty-Mansi Autonomous Okrug. Coll. papers*. V. I. Khanty-Mansiysk, pp. 323–332. (In Russ.)
- Zubkov M.Yu., Vasiliev O.E. (1991). Prospects for oil and gas potential of the pre-Jurassic complex of the Shaim region. In: *Geology and oil and gas content of the Triassic-Middle Jurassic deposits of Western Siberia*. Novosibirsk: SNIIGiMS, pp. 124–137. (In Russ.)

About the Author

Mikhail Yu. Zubkov – Cand. Sci. (Geology and Mineralogy),
Director, West Siberian Geological Center LLC
build. 4/9, 11, Surgutskaya st., Tyumen, 625002, Russian
Federation

Manuscript received 8 May 2020;

Accepted 9 October 2020; Published 11 December 2020