

Original Paper

Geochemistry and formation conditions of the Domanik sediments (Semiluksk horizon) in the Volga-Ural petroleum province, Russia



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ABSTRACT

The study reconstructs the Upper Devonian Domanik sedimentation conditions using geochemical studies. Domanik sediments, the subject of study, are being developed in Russia's Volga-Ural petroleum province. Core samples have been collected from the South Tatar arch and the Birskeya saddle, totaling four wells. Macroscopic description, optical microscopic petrographic examination, X-ray analysis, X-ray fluorescence analysis, inductively coupled plasma mass spectrometry (ICP-MS), simultaneous thermal analyses, scanning electronic microscopy (SEM), Rock-Eval pyrolytic studies, and correlation analysis were among the methods used in the study. Carbonate rocks, carbonate-siliceous rocks enriched with organic matter, and carbonate breccias are the main identified lithotypes. The predominant rock-forming mineral in carbonate-siliceous rocks enriched with organic matter is quartz (chalcedony) of authigenic genesis. The lack of correlation between organic matter concentration and quartz, as well as the results of simultaneous thermal studies and SEM, suggest that quartz is present in both biogenic and chemogenic forms. The proxies Cd/Mo and $\text{Co} \times \text{Mn}$ were used for proving variable hydrodynamic conditions in the Domanik sediments sea: sediments were deposited under both stationary and seasonal upwelling conditions. The major bioproductivity of the Domanik sea was also influenced by hydrothermal activity. The proxy $(\text{Fe} + \text{Mn})/\text{Ti}$ data and the results of the rock genesis evaluation using the Zn-Ni-Co triangle diagram confirm this. The presence of hydrothermal fluids not only improved primary production in the paleobasin, but it additionally provided silica, as evidenced by the strong relationship between silica and exhalation components in carbonate-siliceous rocks. Volcanic activity had a slight impact on Domanik sediment genesis. Anoxia and euxinia in the Domanik sea were indicated by proxy U/Th-TOC and V/Cr-TOC data, as well as behavior of U-EF and Mo-EF on the covariation plot, which influenced organic matter burial in the sediments. Simultaneously, the terrigenous intake was limited. Carbonate breccias, which are common in the Domanik sediments section, developed as a result of the gravitational transfer of carbonate fragments into the carbonate-siliceous material, which might be driven by earthquakes.

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1. Introduction

Due to the depletion of traditional and relatively easily recoverable hydrocarbons, more attention is currently being paid in Russia to the search for and evaluation of relatively new sources of raw materials, e.g., hydrocarbon reservoirs of the Domanik siliceous

rocks. The latter are non-traditional rocks with a high content of organic matter. Putting them into operation necessitates a thorough understanding of their mineralogical, lithological, and geochemical characteristics.

Starting with the works of Arkhangel'sky (1929), the Middle Frasnian Domanik siliceous rocks developed within the eastern part of the Russian plate have been considered oil source rocks for the oil fields in the east of the East European platform, as confirmed by recent studies (Galimov and Kamaleeva, 2015; Stupakova et al., 2015a,b). In Russian-language literature, these rocks are known as

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Domanik sediments since they have been found on outcrops near the Domanik River (Komi Republic, Russian Federation) (Strakhov et al., 1955).

Domanik sediments, which developed on the Volga-Ural petroleum province's territory, are the only regional oil source rocks of carbonate-siliceous composition with a high content of organic matter. They occupy a relatively small thickness within the Paleozoic sedimentary cover of the eastern part of the East European platform and are confined to the Semiluksk horizon of the Frasnian stage of the Upper Devonian (Liang et al., 2020). Their thickness within the Volga-Ural province in the Semiluksk horizon varies between 20 m and 50 m, whereas the overall thickness of the sedimentary cover here is up to 2000 m.

For a long time, it was believed that the Domanik sediments were clay-carbonate-siliceous rocks. However, recently, it has been reliably revealed that the Domanik are carbonate, siliceous, and carbonate-siliceous rocks. The proportion of clay minerals in them rarely exceeds 4% (Stupakova et al., 2017; Khayuzkin et al., 2021). Organic matter is found in the carbonate-siliceous rocks of the Domanik sediments, with a content of 20% or more (Poludetkina et al., 2017; Kayukova et al., 2017).

Domanik sediments are thought to be unique rocks (Maximov and Rodionova, 1981; Machulina, 2018). This is due to numerous factors, among them the limited distribution of these sediments over the Volga-Ural petroleum province and, in the overall sedimentary section of the region, the siliceous-carbonate mineral composition, the fine-grained structure, as well as the presence of many metals and their enrichment in the organic matter. The fact that Domanik sediments are named “mixtites” or “mixed rocks” emphasizes their distinctiveness (Kontorovich et al., 2016). This demonstrates the occurrence of genetically distinct components in sediments.

According to literature data, at least three factors influence the formation of the Domanik siliceous rocks: 1) increased the sedimentation basin's bioproductivity; 2) the anoxic conditions in the lower layers; and 3) the limited terrigenous flows (Hodgskiss et al., 2020; Deng et al., 2019; Jin et al., 2020). The anoxic conditions in the near-bottom layers of the paleobasin and the limitation of terrigenous flows in the Domanik basin are documented by many researchers (Bushnev, 2009; Stupakova et al., 2017). At the same time, there is no consensus on the mechanism for increasing the bioproductivity in the paleobasin or the supply of silica to the Domanik depositional basin.

Some publications documented the influence of endogenous factors on the genesis of the Domanik sediments (Baturin, 2009; Gottikh and Pisotsky, 2017; Liang et al., 2020). This is indirectly verified by studies on the influence of endogenous fluids on the sediment's formation, which have a high proportion of sapropelic organic matter (Belenitskaya, 2008; Tsekhovsky et al., 2018). However, the same publications show that organic-rich sediments can form in the absence of terrigenous material or at a slower rate of sediment accumulation without the effect of endogenous fluids.

Maksimova (1970) concluded that the silica minerals in the Domanik sediments are volcanic in character based on the presence of volcanic rocks and their fragments in layers of the same Domanik sediment age. The same study mentions the Domanik sea's regular changes in redox potential and, presumably, the influence of an endogenous factor on the formation of such rocks (Maksimova, 1970). There is no solid evidence to support this. In another work devoted to studying the Domanik sediments in the Mukhanovo-Erokhov trough, the researcher documented the presence of ash layers up to 2 cm thick in the section (Shakirov et al., 2022). Their impact on the Domanik genesis is difficult to assess since the proportion of ash layers per 1 m of core does not exceed 3%.

In other works, for example, Strakhov (1960) concludes that the

Domanik basin was characterized by normal salinity and a normal oxygen regime based on a study of the ratio of various types of fauna. In Strakhov's opinion, the formation of Domanikites took place under conditions of the periodic blooming of plankton and, accordingly, the entry of organic matter into the sediments. The flourishing of plankton is due to the periodicity of the implementation of the vertical circulation of seawater (upwelling), which is associated with meteorological factors.

The author's conclusions are not supported by any researchers. Thus, questions about the influence of the possible role of upwelling, endogenous, and volcanogenic factors in the formation of Domanikites and the reasons for the increased content of silica and organic matter remain largely unclear. The present publication is devoted to the solution of these questions.

2. Geological setting

Domanik-type sediments, or Domanikites, are common in the Volga-Ural and Timan-Pechora petroleum provinces of the East European Platform. They form a meridionally elongated strip extending to the west from the Ural Mountains (Kiryukhina et al., 2013) (Fig. 1(a)).

Stratigraphically, Domanik sediments are found, starting with the Semiluksk horizon (Fig. 2(b)). They are distributed over most of the territory within the boundaries of the Semiluksk horizon (Morozov et al., 2022). The thickness of the sediments within its stratigraphical boundaries is approximately 30 m. Within the Kama-Kinel trough system, a structure formed in the Frasnian stage of the Late Devonian on the territory of the Volga-Ural province, Domanik sediments are found up to the Early Tournaisian, and their thickness can reach between 300 and 350 m. The present depth of Domanik sediments in the territory of the Volga-Ural petroleum province varies from 1500 to 3000 m.

According to recent concepts, Domanik sediments accumulated in the equatorial zone under conditions of a deep-water shelf, near the boundary of the continental slope (Fig. 1(b)). The Domanik sediments were formed under conditions of maximum transgression for the Semiluksk time (Liang et al., 2015) and a low-energy environment (Savel'eva, 2010).

3. Materials and methods

3.1. Materials

The research used core samples from four wells located in the central part of the Volga-Ural petroleum province (Fig. 2(a)). The core recovery rate in all the wells was 100%. Sediments of the Domanik (Semiluksk horizon) of the Middle Frasnian of the Upper Devonian were penetrated in the territory of the South Tatar arch and the Birska saddle by the drilled wells (Fig. 2(a)).

Prior to sampling and performing the analytical work, a macroscopic description of the pre-sawn core was carried out. Sampling was carried out systematically every 0.3–0.6 m of the core for each well. Mostly dark grey and black samples enriched with organic matter (Domanik sediments) were chosen. In total, 120 samples were collected from the studied wells as follows: for well 1, 23 samples were collected at a depth of 1785.3–1796.0 m. For well 2, 22 samples were collected at a depth of 1723.0–1733.0 m. 45 samples were collected from well 3 at a depth of 1700.0–1727.0 m, while 30 samples were collected from well 4 at a depth of 1616.0–1642.0 m. The location of the studied wells is shown in Fig. 2(a). Representative photographs of cores and samples are shown in Fig. 3.

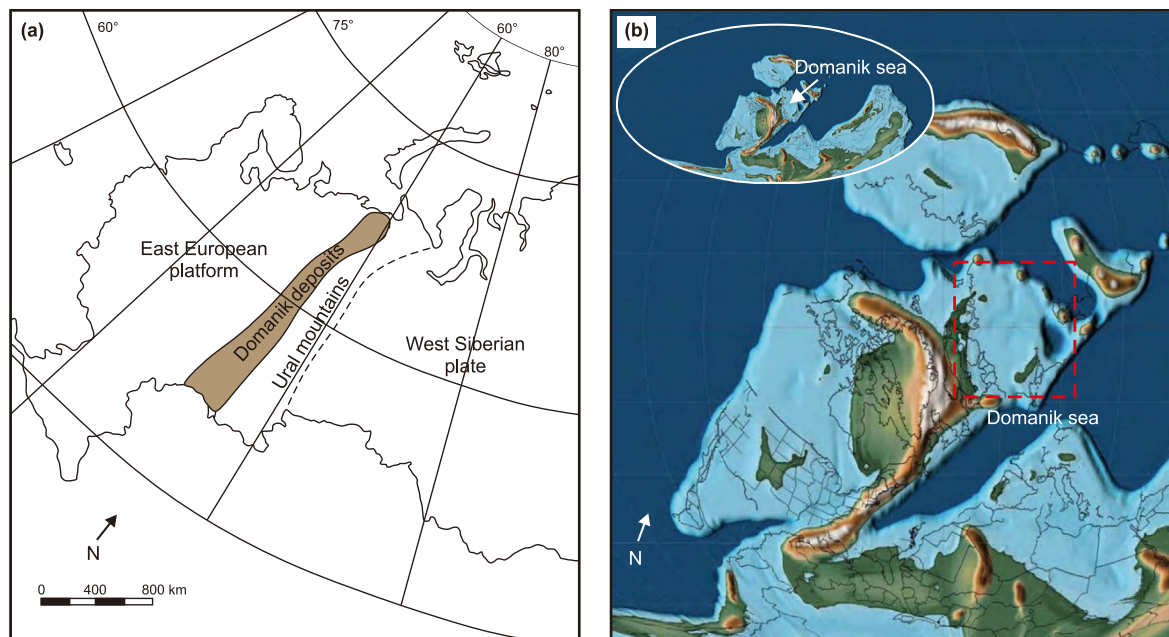


Fig. 1. A plat showing: (a) Distribution map of the Domanik sediments within the western part of the Russian Federation. (b) Paleogeographic reconstruction of the Domanik sedimentary conditions (Scotese, 2001).

3.2. Methods

Optical-microscopic, X-ray diffraction (XRD), scanning electron microscopic (SEM), X-ray fluorescence, synchronous thermal analyses, pyrolytic studies using the Rock-Eval method, and geochemical studies using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method were the research methods. All research was conducted at Kazan Federal University's Institute of Geology and Oil and Gas Technologies in Russia.

3.2.1. Macroscopic description of core materials

To reveal the lithological composition and heterogeneity of the cored materials and to determine the sequence of stratification of certain lithotypes, a macroscopic description of the pre-sawn core was performed. A total of 73.7 m of the core materials were described.

3.2.2. Optical microscopic petrographic analysis

The thin sections were optically examined using an optical polarizing microscope of transmitted light “Axio Imager” (Carl Zeiss, Germany), equipped with a camera. A total of 60 thin sections were prepared and petrographically examined. The carbonate texture has been described based on Dunham's (1962) classification.

3.2.3. X-ray analysis

An X-ray diffractometer (Bruker D2 Phaser, Germany) was used for the X-ray analysis. A few milligrams of the sample were ground using a hand mill prior to performing the analysis. During the experiment, a Brega-Brentano geometry was used using monochromatic CuK radiation in step scanning mode. When deciphering the diffraction patterns, we used the international card index of powder X-ray diffraction standards, PDF-2 ICDD. The determination of the qualitative mineral composition was carried out in the DIF-FRAC plus program evaluation package-EVA Search/Match. When determining the quantitative composition, the Topas program was used. The mineralogical composition of a total of 120 samples was

determined using XRD analyses.

3.2.4. X-ray fluorescence analysis

The chemical composition of the studied samples was determined using X-ray fluorescence analysis using the S8 Tiger wave-dispersive X-ray fluorescence spectrometer (Bruker, Germany). The spectra collected were analyzed using the software Bruker Spectra Plus WDX and Bruker AXS Eval 2. A total of 120 samples were analyzed using X-ray fluorescence analysis.

3.2.5. Geochemical studies using the ICP-MS method

The inductively coupled plasma mass spectrometry (ICP-MS) method, based on a mass spectrometer with inductively coupled plasma iCAP Qc (Thermo-Fisher Scientific, Germany), was used to determine the concentrations of the small chemical elements in the studied rocks. To suppress the polyatomic spectral overlaps, the preparations were investigated in the KED mode using a helium reaction-collision cell with kinetic energy discrimination. The limit of detection (LO) of elements was calculated using the 3S-criterion based on the results of five measurements of the control sample. The mass spectrometer was pre-calibrated with multi-element standards ranging in concentration from 1 to 1000 ppm (parts per billion) for each element. In total, 10 samples were examined using the inductively coupled plasma mass spectrometry method.

3.2.6. Correlations analyses

The correlations between mineral, chemical, and organic components in the studied rocks were determined using correlation analysis. The analysis was conducted by importing research results into MS Excel and assessing datasets with the Correl tool.

3.2.7. Simultaneous thermal analyses

The method of synchronous thermal analysis was employed to investigate the thermophysical properties of the studied samples, yielding two curves: a differential calorimetry (DSC) curve and a thermogravimetric (TG) curve. The measurements were taken with an STA 443 F3 Jupiter instrument from Netzsch (Germany) and the

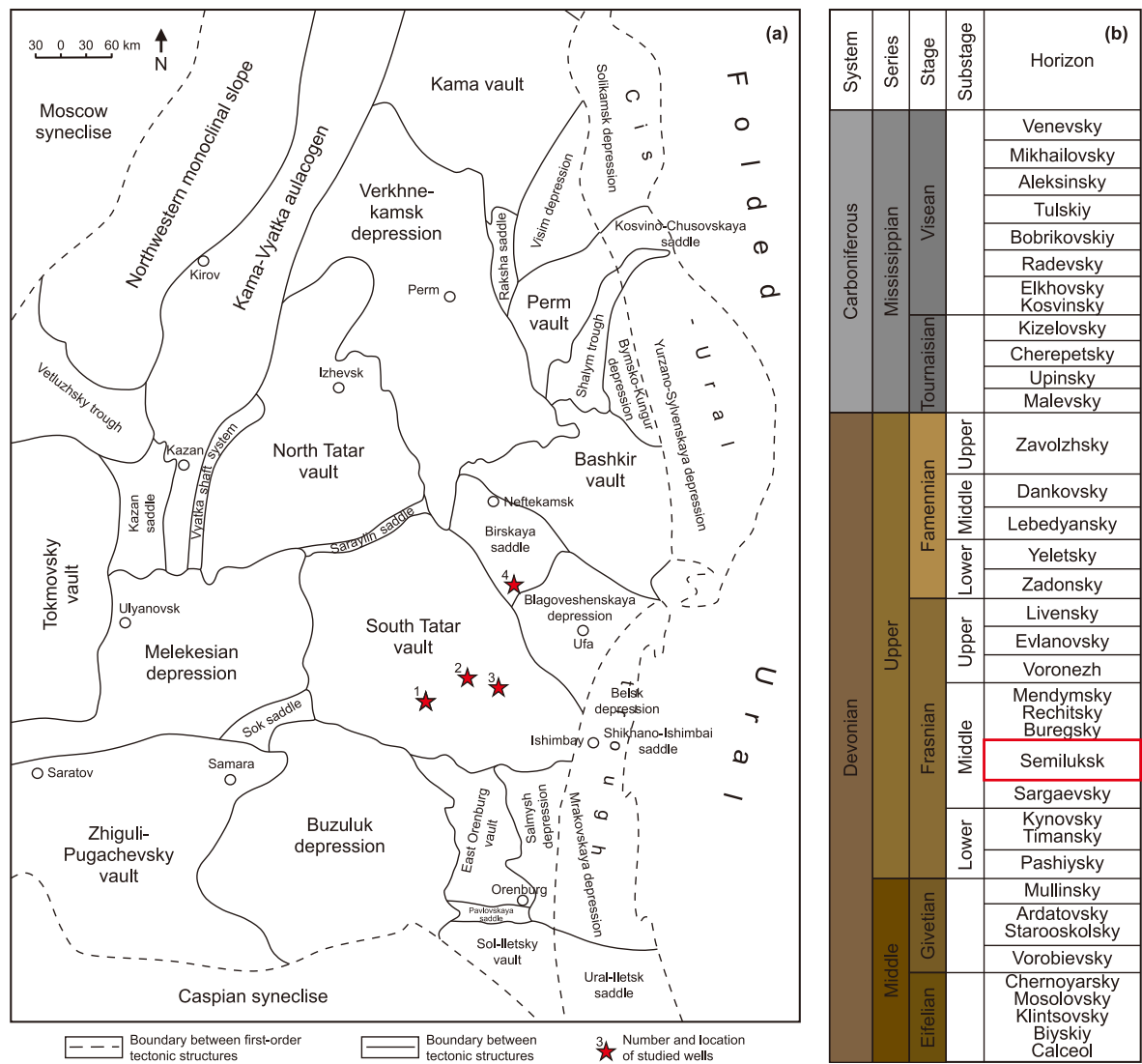


Fig. 2. A plat showing: (a) Tectonic scheme of the Volga-Ural petroleum province indicating the locations of the studied wells. (b) Regional stratigraphic column of the Devonian and Carboniferous systems.

Netzsch software Proteus thermal analysis. Temperatures in the range of 30–1000 °C in the air were measured. A total of five samples were analyzed.

3.2.8. Scanning electron microscopic analysis

An XL-30ESEM scanning electron microscope (FEI, Philips, Netherlands) equipped with an EDAX energy-dispersive spectrometer (USA) was used for the electron microscopic study. The samples were collected in the topographic contrast mode (SE detector, secondary electrons) at a 20 keV accelerating voltage. As preparation, fresh chipped samples coated with carbon were used. A total of ten samples were studied.

3.2.9. Pyrolytic studies using the Rock-Eval method

Pyrolytic studies using the Rock-Eval method were conducted to determine the quality and quantity of organic matter contained in the studied rocks. Pyrolytic studies were carried out on a PY-3030D pyrolytic cell in a mode similar to measurements performed on a Rock-Eval 6 instrument in Bulk Rock mode using an Agilent 5977B mass spectrometric detector (Chemodanov et al., 2019). A total of 30 samples were studied.

3.2.10. Calculation of enrichment factors (EF)

To calculate the enrichment factors of Mo and U in the studied samples, trace metal concentrations are given in the form of enrichment factors (EFs), which were calculated as:

$$X_{EF} = [(X/Al)_{sample}/(X/Al)_{PAAS}] \tag{1}$$

where *X* and *Al* represent the weight percent concentrations of elements *X* and *Al*, respectively. In the present study, samples were normalized using PAAS data (Taylor and McLennan, 1988).

4. Results

4.1. Lithofacies

The macroscopic investigations showed that the studied sections are composed of alternating carbonate and carbonate-siliceous rocks, which form horizontal beddings. The layer's thickness can vary from a few millimeters to a few tens of centimeters. The boundaries of lithofacies are sharp, as shown in Fig. 3(a)–(c). The proportion of carbonate and carbonate-siliceous layers in the

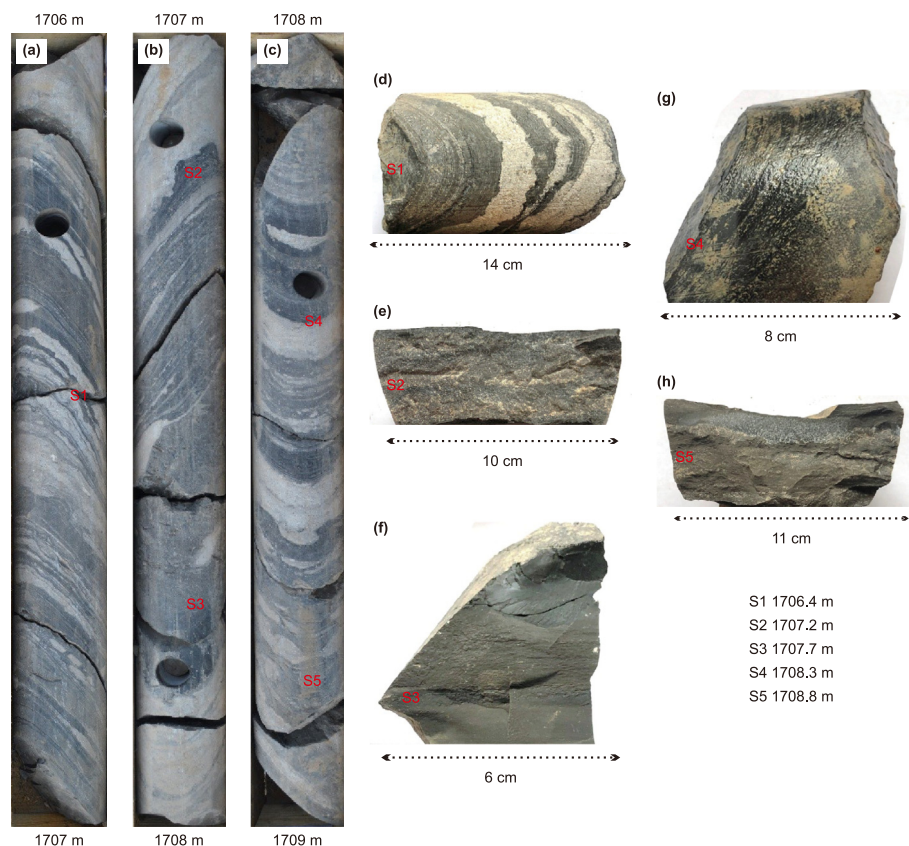


Fig. 3. A plate showing: (a)–(c) Representative core photographs from well 3 show interbeds of carbonate (in light colours) and carbonate siliceous rocks (in dark colours) in the Domanik sediments. The sediments in the core photographs look cross-bedded due to the deviated well drilling. Sampling locations on Fig. 3(a)–(c) are referred to as S1, S2, etc. (d)–(h) Representative core sample photographs showing carbonate and carbonate siliceous rocks. See the well location in Fig. 2(a).

cored section of different wells can vary significantly. Thus, among the studied Domanik sediments (Semiluksk horizon), three major lithofacies were identified, including carbonates (limestone), carbonate-siliceous rocks, and carbonate breccias. The predominance of either carbonates or carbonate-siliceous rocks is often observed. Carbonate breccias are rare in sections; nevertheless, such rocks were found in the studied wells. Each of the distinct facies is explained below.

4.1.1. Limestones

Macroscopically, the limestone is pale in color and characterized by a hidden grain structure. Organic matter is not detected optically. Based on Dunham's classification (Dunham, 1962), two types of limestone recognized are mudstone and wackestone (Fig. 4(a) and (b)). According to optical-microscopic examinations, the structure of mudstones is micritic, and the texture is predominantly uniform. The rocks are 99% composed of adjoining xenomorphic calcite grains varying in size between 0.01 and 0.05 mm, and 1% are authigenic chalcedony grains of up to 0.05 mm in size, forming a dense intergrowth aggregate (Fig. 4(e) and (f)). There are organic remnants (from 5 up to 10%) of poor and moderate preservation, varying in size from 0.25 to 1.0 mm, represented by scattered shells of ostracods, calcispheres, and calcitized algae. Under the microscope, porosity is not detected. The difference between wackestone and mudstone resides in the larger amount of bioclasts. However, their occurrence in the studied rocks is substantially less than in mudstones.

4.1.2. Carbonate-siliceous

The carbonate-siliceous rock's color is controlled by the presence of organic matter and varies from dark grey to virtually black. The texture is predominantly homogeneous, and the rocks are generally dense (Fig. 4(c)). According to optical-microscopic studies (Fig. 4(g)), the rocks' structure is pelitic, and the texture is uniform. In the thin section's photomicrographs, the rocks are composed of quartz of chalcedony size, which forms a dense aggregate intergrowth with the xenomorphic calcite grains. Clay material and feldspars with a diameter of less than 0.01 mm were also recorded. Authigenic pyrite content is less than 1%. These minerals are equally dispersed in the rock mass among the organic matter, which forms microlayers about 0.05 mm thick. Bioclast remains rarely observed, represented by the shells of radiolarians and tentaculites. Rhombohedral grains of secondary dolomites are sometimes encountered.

4.1.3. Carbonate breccias

They form layers up to 0.5 m thick and sometimes more. No regularity in their distribution in the core sections of the studied wells was observed. They are characterized by a clear breccia structure, and the size of light carbonate fragments is up to several centimeters (Fig. 4(d)). The fragments are enclosed in a dark carbonate-siliceous mass. According to the optical-microscopic studies (Fig. 4(h)), carbonate fragments are represented to variable degrees by angular and usually continuous fragments of mudstone, less often wackestone. They are cemented with carbonate-siliceous material enriched with organic matter. Among the minerals, quartz (chalcedony) and calcite were observed;

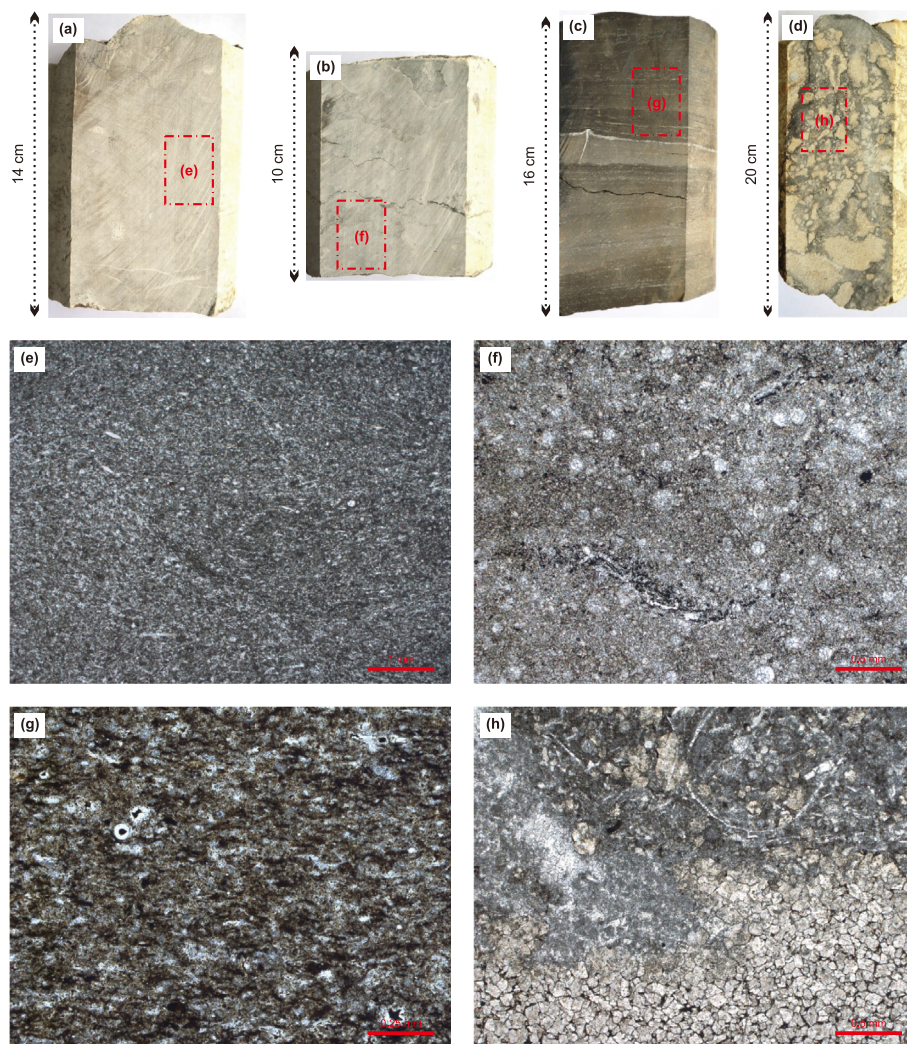


Fig. 4. Representative core sample photographs from the Domanik sediments showing: (a), (b) Limestone, pale in color and characterized by a hidden grain structure. (c) Horizontally stratified carbonate-siliceous rocks. (d) Carbonate breccias with light carbonate fragments up to several centimeters in size and enclosed in the dark carbonate-siliceous mass. Representative optical photomicrographs showing: (e), (f) Mudstone and wackestone composed of calcite grains varying in size between 0.01 and 0.05 mm, scattered shells of ostracods, calcispheres, and calcitized algae were also presented. (g) Carbonate-siliceous (mudstone) composed of dense aggregate of quartz (chalcedony) intergrowth with the calcite grains and rare bioclast remains. (h) Carbonate breccias composed of mudstone fragments cemented with carbonate-siliceous material enriched with organic matter, quartz (chalcedony), and calcite were observed. Grains of dolomite and pyrite were also observed.

rhombohedral grains of dolomite up to 0.25 mm in size and an admixture of pyrite were also observed. Under the microscope, the rocks are dense, and the porosity is not detected.

4.2. X-ray analysis

The results of X-ray analysis are the diffraction patterns of samples from the Domanik sediments, which were used to determine the mineral composition. The average mineral composition of each lithotype in each well was determined. Table 1 shows the results of the X-ray analysis.

According to the obtained results, calcite forms monomineral rocks-limestone (mudstone and wackestone). Calcite and quartz are the primary minerals in the carbonate-siliceous rocks. When the average values were calculated, potassium feldspar was found to be a rock-forming mineral in the carbonate-siliceous rocks. In practice, potassium feldspar, dolomite, mica, and pyrite are frequently recorded as impurities. The distribution of minerals in the identified lithotypes is shown in Fig. 5.

The results of X-ray studies of the carbonate-siliceous rocks were processed to identify the correlations. The results of the correlation are shown in Table 4.

4.3. X-ray fluorescence analysis

X-ray fluorescence analysis was performed to assess the elemental composition of the carbonate-siliceous rocks enriched in organic matter. Results are presented in Table 2.

The value "0" in Table 2 corresponds to a value below the threshold minimum and is controlled by the instrument's resolution. According to the results obtained, the main petrogenic compounds of the carbonate-siliceous rocks are SiO_2 , CaO , SO_3 , Al_2O_3 , K_2O , and Fe_2O_3 , which is consistent with the mineral composition of the rocks.

4.4. Geochemical studies using the ICP-MS method

With the help of ICP-MS, the contents of fine elements in the

Table 1
Mineral composition of the Domanik sediments (Semiluksk horizon) in the studied wells.

Rocks/minerals	Quartz	Calcite	Dolomite	K-feldspar	Mica	Pyrite	Total
Limestones, average for							
Well 1	1.3	97.3	1.0	0.0	0.0	0.4	100.0
Well 2	0.0	99.0	0.0	0.0	0.0	1.0	100.0
Well 3	2.1	94.1	3.0	0.0	0.0	0.8	100.0
Well 4	1.5	97.4	0.0	0.0	0.0	1.1	100.0
All wells	1.2	96.7	1.2	0.0	0.0	0.9	100.0
Carbonate-siliceous rocks, average for							
Well 1	48.2	36.3	1.8	7.4	4.7	1.6	100.0
Well 2	59.7	25.3	2.8	5.1	5.6	1.5	100.0
Well 3	51.7	33.1	3.1	5.8	4.5	1.8	100.0
Well 4	64.8	19.7	2.5	6.5	4.4	2.1	100.0
All wells	56.1	28.6	2.6	6.2	4.8	1.7	100.0
Carbonate breccias, average for							
Well 1	9.3	67.2	22.9	0.0	0.0	0.6	100.0
Well 2	3.5	78.1	18.4	0.0	0.0	0.0	100.0
Well 3	7.5	63.7	17.4	6.1	4.2	1.1	100.0
Well 4	3.2	80.5	16.3	0.0	0.0	0.0	100.0
All wells	5.9	72.4	18.8	1.5	1.0	0.4	100.0

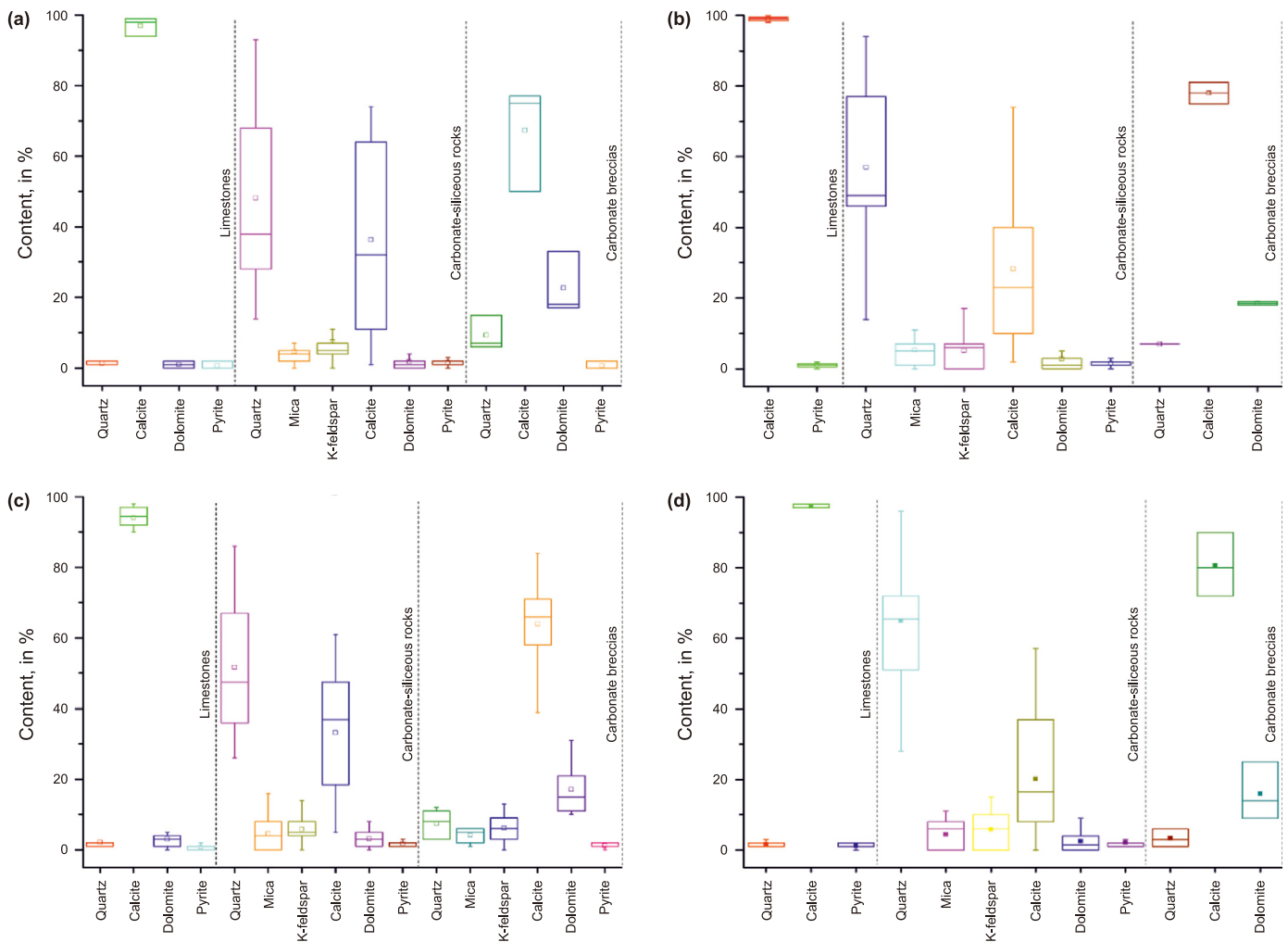


Fig. 5. Box-charts of mineral distribution inside well interval: (a) Well 1, (b) Well 2, (c) Well 3, (d) Well 4. Boundary of the box characterises 25% deviation from the mean value.

carbonate-siliceous rocks enriched in organic matter were revealed. The results are shown in Table 3. The content of such

elements as Tantalum (Ta), Tungsten (W), Osmium (Os), Iridium (Ir), Platinum (Pt), Gold (Au), Ruthenium (Ru), Rhodium (Rh),

Table 2
Elemental composition of the Domanik sediments (Semiluksk horizon) in the studied wells.

Well	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl
1	0.081–0.165	0.247–0.678	0.53–5.64	14.82–86.99	0.199–0.993	1.001–9.881	0.085–0.21
2	0.116–0.169	0.277–0.521	0.4–2.63	3.07–81.06	0.116–0.937	0.799–2.414	0.093–0.484
3	0.081–0.168	0.148–2.261	0.61–5.79	9.869–83.87	0.785–0.842	0.785–8.62	0.049–0.164
4	0.149–0.461	0.046–0.383	0.546–3.244	29.68–88.98	0.066–0.325	1.04–7.68	0.139–0.413
Well	K ₂ O	CaO	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	Fe ₂ O ₃	NiO
1	0.216–1.992	3.17–30.7	0.03–0.307	0.028–0.763	0–0.1013	0.904–2.1	0.008–0.129
2	0.176–1.147	0.127–52.97	0–0.131	0–0.989	0–0.0393	0.328–1.12	0.005–0.034
3	0.119–2.544	5.294–45.05	0–0.252	0–0.318	0–0.0284	0.269–2.79	0.007–0.077
4	0.101–1.23	0.53–23.32	0–0.169	0.042–0.417	0–0.0166	0.4–1.112	0.013–0.075
Well	CuO	ZnO	SrO	ZrO ₂	MoO ₃		
1	0.0094–0.0356	0.022–0.16	0.008–0.053	0–0.0076	0–0.151		
2	0.059–0.0135	0.0109–0.08	0.009–0.038	0–0.0135	0–0.018		
3	0.0074–0.0335	0.008–0.143	0.016–0.054	0–0.013	0–0.109		
4	0.0074–0.022	0.01–0.139	0–0.0254	0–0.0165	0.009–0.029		

Table 3
Selected trace element compositions (in ppm) and for core samples from studied wells.

Well	Sample	Depth, m	Li	Be	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb			
1	2	1785.9	29.3	1.5	1.6	162.4	417.3	19.8	57.0	8622.6	1.4	94.7	62.5	261.6	2.1	10.2	1.2	4.7			
1	10	1789.7	1.1	0.4	0.4	102.6	136.5	6.4	32.6	2404.1	0.6	58.2	26.4	39.6	0.7	4.5	0.2	2.5			
1	15	1792.2	5.8	3.7	1.6	313.9	72.8	12.4	133.5	9921.9	16.1	33.3	54.5	27.7	3.0	14.0	1.9	9.3			
2	4	1724.8	20.8	2.2	5.6	1403.7	927.9	61.5	54.1	9457.9	8.5	250.7	190.9	340.2	4.7	17.0	2.5	45.0			
2	19	1732.2	28.3	0.5	0.5	126.9	357.9	15.5	44.1	6921.7	1.1	123.2	51.8	123.5	1.1	8.9	0.3	4.0			
3	4	1701.9	25.7	1.1	9.9	1720.4	150.8	138.3	63.8	16680.0	4.8	380.9	197.3	741.4	10.0	17.6	5.0	49.5			
3	7	1704.1	29.4	2.2	9.4	1647.1	199.2	176.1	39.3	12315.5	5.0	582.4	245.4	1065.7	10.2	24.7	7.0	52.9			
3	14	1708.1	14.1	1.9	4.7	784.7	389.6	65.1	29.9	8831.6	6.8	226.3	118.6	433.4	5.4	19.1	3.0	22.6			
4	21	1637.1	10.8	2.5	5.3	941.9	825.8	54.2	49.4	18171.5	44.4	387.5	143.4	378.7	6.3	66.0	5.4	25.2			
4	30	1641.4	13.5	1.0	0.7	143.6	84.4	15.9	38.8	5398.8	1.2	43.9	37.7	70.0	1.0	6.0	0.6	3.8			
Sr	Y	Zr	Nb	Mo	Cd	Sb	Cs	Ba	La	Ce	Pr	Nd	Sm	Gd	Yb	Lu	Hf	Tl	Pb	Th	U
39.4	10.0	18.6	1.1	27.0	5.0	5.4	0.4	10.2	5.7	6.0	1.3	5.5	1.2	1.4	0.7	0.1	0.6	0.5	2.9	0.5	12.7
242.3	5.0	5.7	0.5	8.6	0.8	0.9	0.1	8.6	2.6	2.2	0.5	2.1	0.5	0.6	0.4	0.1	0.1	0.1	1.7	0.2	3.6
282.1	16.9	20.0	1.4	13.9	0.4	0.8	0.6	32.8	12.1	16.6	2.1	9.0	1.6	2.1	1.0	0.1	0.4	0.8	3.3	0.9	8.3
161.4	23.9	47.2	5.9	32.1	6.1	9.6	1.6	113.4	15.0	19.5	3.4	14.8	3.0	3.4	1.6	0.2	1.2	0.9	9.7	3.5	13.2
16.5	7.4	11.2	0.5	36.9	2.8	5.7	0.4	15.1	3.0	3.0	0.6	3.1	0.7	0.9	0.4	0.0	0.2	0.2	2.3	0.4	6.9
334.7	71.3	66.2	6.2	7.2	1.4	3.1	3.0	119.9	40.6	35.0	8.6	38.0	8.3	9.6	4.1	0.6	1.9	1.1	6.6	5.0	14.0
193.3	79.5	69.0	6.0	11.9	1.9	3.8	3.2	115.9	42.8	33.7	9.3	42.2	9.2	11.1	4.0	0.5	2.0	1.0	7.4	5.7	17.2
260.7	46.1	28.9	2.7	32.3	3.2	6.0	1.2	44.7	21.4	16.5	4.0	18.5	3.8	5.1	2.3	0.3	0.7	1.1	5.4	2.4	14.8
199.3	54.4	50.8	3.5	227.6	6.0	18.5	1.3	64.0	28.3	25.6	5.3	23.9	5.0	6.3	2.7	0.4	1.0	4.0	13.9	2.6	55.7
41.5	9.2	12.0	0.6	7.0	0.5	0.7	0.2	11.4	5.1	3.8	0.9	4.1	0.9	1.1	0.5	0.1	0.2	0.1	1.1	0.4	2.3

Palladium (Pd), Silver (Ag) and Tin (Sn) in the studied wells turned out to be below their threshold values.

4.5. Correlation analysis

Correlation analysis was performed based on the results of X-ray and X-ray fluorescence analyses in order to identify relationships in the distribution of minerals and petrogenic compounds in the carbonate-siliceous rocks enriched in organic matter. The results of the correlation analysis of the mineral composition of the Domanik sediments are shown in Table 4.

According to the obtained results, weak, medium, and strong

bonds between minerals were found. A moderately positive relationship is found between feldspar, mica, and pyrite; a moderately negative relationship is found between quartz and mica, calcite and feldspar, and calcite and pyrite. There is a strong negative relationship between quartz and calcite. The results of the correlation analysis of petrogenic elements are shown in Table 5. The analysis revealed a paragenetic group of compounds characterized by moderate, noticeable, and high positive bonds: Al₂O₃, K₂O, Fe₂O₃, NiO, CuO, ZnO, ZrO₂, and TiO₂. In addition, the results of the analysis show the presence of a negative relationship between SiO₂ and CaO, which is consistent with the results of the correlation analysis of the mineral composition of the sediments.

4.6. Simultaneous thermal analysis

Synchronous thermal analysis was performed to determine the thermophysical properties of quartz in the carbonate-siliceous rocks. The diagrams below (Fig. 6) show differential scanning calorimetry (DSC) and thermogravimetry (TG) curves. The black curve can be used to judge the mass loss associated with the oxidation of organic matter and phase transitions of minerals in the samples; the blue curve can be used to identify reactions that occur with

Table 4
Minerals correlation coefficients of the Domanik sediments (Semiluksk horizon).

Minerals	Quartz	Calcite	Dolomite	K-feldspar	Mica	Pyrite
Quartz	1.00	−0.79	−0.25	−0.14	−0.32	−0.06
Calcite	−0.79	1.00	−0.04	−0.37	−0.23	−0.31
Dolomite	−0.25	−0.04	1.00	0.03	0.26	−0.02
K-feldspar	−0.14	−0.37	0.03	1.00	0.48	0.68
Mica	−0.32	−0.23	0.26	0.48	1.00	0.45
Pyrite	−0.06	−0.31	−0.02	0.68	0.45	1.00

Table 5
Correlation coefficients between petrogenic elements in the Domanik sediments (Semiluksk horizon).

Components	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂
SiO ₂	0.31	−0.57	−0.27	1.00	0.16	−0.32	0.02	−0.34	−0.52	−0.29
CaO	−0.35	0.51	−0.06	−0.52	−0.13	−0.13	−0.50	−0.12	1.00	−0.12
Na ₂ O	1.00	−0.36	−0.12	0.31	−0.58	0.01	0.62	−0.16	−0.35	−0.15
MgO	−0.36	1.00	0.26	−0.57	−0.06	−0.05	−0.31	0.27	0.51	0.24
Al ₂ O ₃	−0.12	0.26	1.00	−0.27	0.27	0.59	−0.17	0.97	−0.06	0.96
K ₂ O	−0.16	0.27	0.97	−0.34	0.32	0.56	−0.12	1.00	−0.12	0.95
Components	V ₂ O ₅	Cr ₂ O ₃	Fe ₂ O ₃	NiO	CuO	ZnO	SrO	ZrO ₂	MoO ₃	
SiO ₂	−0.25	0.52	−0.27	−0.20	−0.24	−0.17	−0.75	−0.12	−0.05	
CaO	−0.21	−0.31	−0.23	−0.25	−0.12	−0.18	0.42	0.03	−0.26	
Na ₂ O	0.07	−0.27	−0.28	−0.03	−0.11	−0.01	−0.46	0.06	−0.08	
MgO	−0.06	−0.26	−0.02	0.05	0.14	0.00	0.70	−0.03	−0.08	
Al ₂ O ₃	0.27	−0.21	0.57	0.75	0.86	0.64	0.32	0.55	0.35	
K ₂ O	0.28	−0.17	0.62	0.71	0.82	0.61	0.35	0.48	0.29	

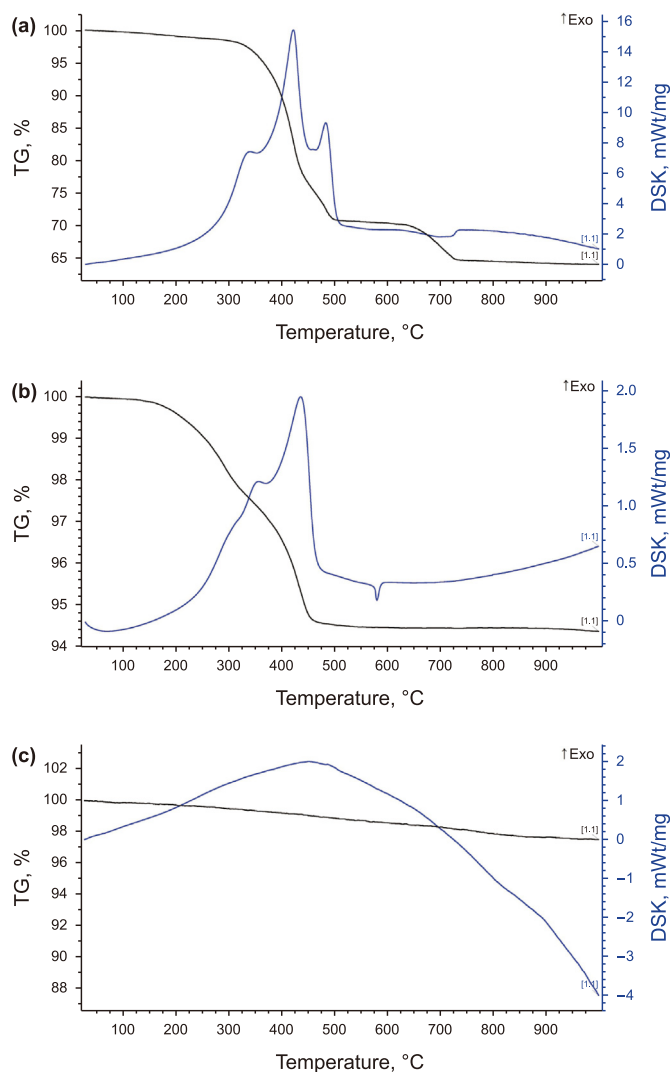


Fig. 6. Representative DSC and TG curves of simultaneous thermal analysis. (a) Carbonate-siliceous rocks of the Domanik sediments (Well 1, sample 4); (b) Bituminous polymictic sandstone (reservoir rock, Romashkino oil field, Republic of Tatarstan, Russia); (c) Technical jasper sample.

minerals with absorption or release of energy (exo and endo effects). Five samples from the carbonate-siliceous rocks enriched in organic matter and containing at least 50% quartz were studied.

Below (Fig. 6) are representative diagrams of the DSC and TG curves of the studied carbonate-siliceous rocks, polymictic sandstone, the study of which was carried out earlier, outside of this study, and the technical jasper.

The studied carbonate-siliceous rock samples are characterized by mass loss with increasing temperature (from 20 to 900 °C) (Fig. 6(a)). The presence of an endothermic effect in the temperature range of 300–600 °C on the DSC curve of the rock sample is explained by the thermal dissociation of carbonates (Fig. 6(a)). The organic matter (OM) content in the carbonate-siliceous rocks was estimated from the mass loss of the samples in the temperature range of 200–600 °C (Fig. 6(a)), since at temperatures from 20 to 200 °C, the adsorbed water is removed and volatile hydrocarbons evaporate from the rock; losses above 650 °C are associated, as mentioned above, with the destruction of carbonate minerals. The most significant weight loss of the sample occurs in the temperature range of 400–600 °C, which is associated with the destruction of high-molecular-weight bituminous components and insoluble kerogen, i.e., that part of the OM that was not transformed in natural maturation processes to the stage of oil generation.

4.7. Scanning electron microscopic analysis

Studies under the electron microscope were carried out only on carbonate-siliceous rocks enriched in organic matter. The obtained results show that the carbonate-siliceous rocks are composed of fine-to-micro-grained carbonate-aluminosilicate masses.

Larger grains of calcite, up to 2 μm in size, are observed. The grain size of the quartz (chalcedony) is usually less than 5 μm; the grains are isometric, and they are not cleaved. The aggregates are uniformly granular. No clastic quartz is found (Fig. 7(a) and (b)). The rocks rarely contain well-faceted, partially corroded K-feldspar crystals (Fig. 7(c)) and thin mica flakes (Fig. 7(d)). Pyrite crystals often form frambohedra (Fig. 7(e)), which occur sporadically and are isolated in the form of irregular shapes up to 50 μm in size, indicating the process of recrystallization.

In the studied Domanik sediments, kerogen is often found under SEM. Clots and interlayers form isometric and oblong shapes up to 10–20 μm. Porosity in kerogen is not detected (Fig. 7(f)).

The study of rocks under an electron microscope showed that even at high magnifications, only insignificant subcapillary pores, up to 5 μm in size, are distinguished. Single-pore channels of insignificant length are sometimes observed. Moreover, such channels have a small length, are single, and are not interconnected. Such channels do not have any significance in ensuring the filtration characteristics of rocks.

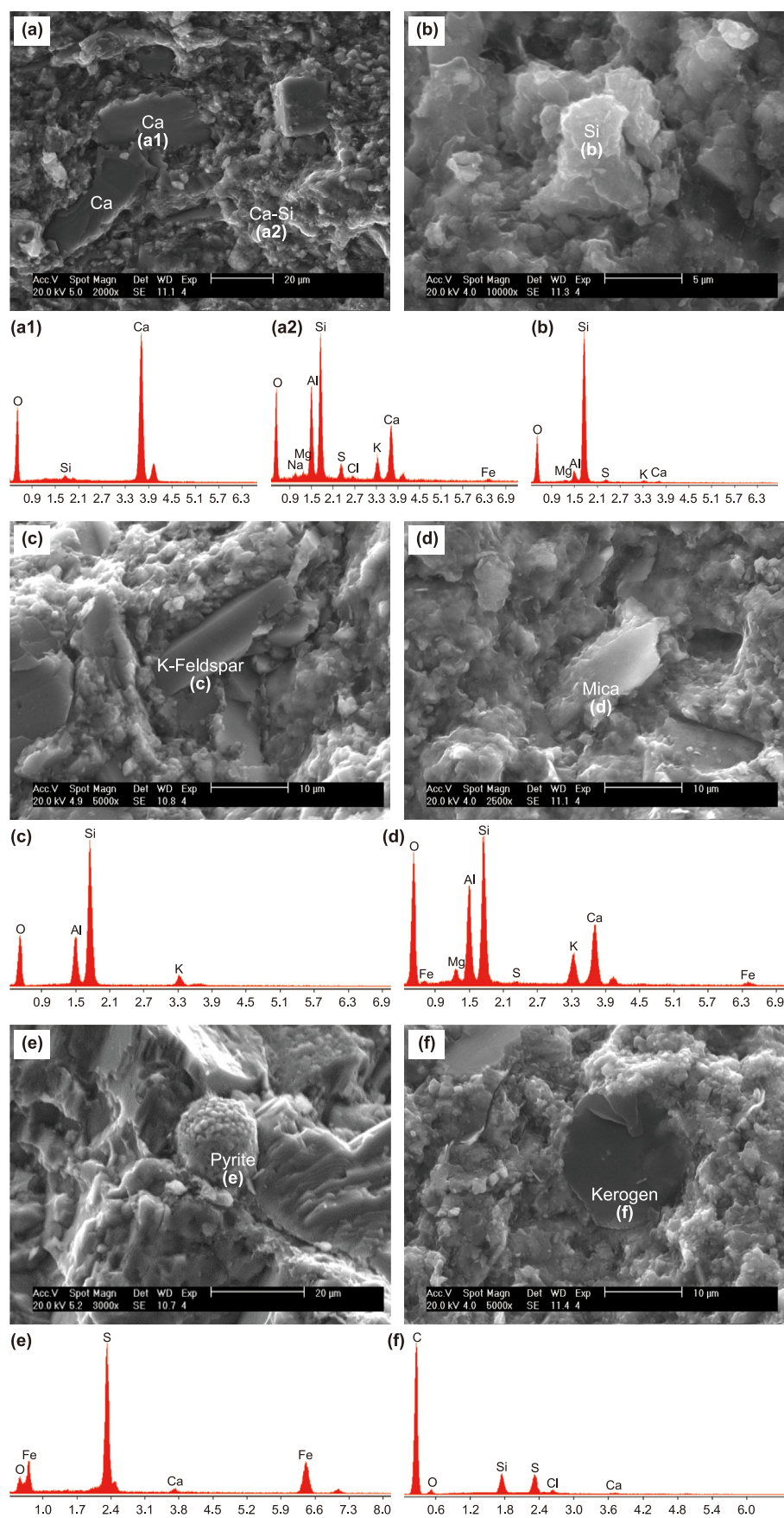


Fig. 7. Structure and morphology of the carbonate-siliceous rock minerals under the electron microscope.

4.8. Pyrolytic studies using the Rock-Eval method

Pyrolytic studies were carried out on 30 samples. Analysis showed that the studied sediments are characterized by a high content of hydrocarbons with residual oil generation potential (parameter S2, mean 34.13 mg/g) and a low proportion of free, mobile hydrocarbons (parameter S1, mean 1.96 mg/g) (Figs. 8 and 9). For all studied samples, the degree of affinity of organic

matter and its type were studied. It was found that organic matter extracted from rocks corresponds to type II organic matter (Tissot and Welte, 1978). The studied samples showed that they are also characterized by the highest temperatures for the maximum yield of hydrocarbons (parameter T_{max}). However, for all the studied samples, the organic matter belongs to the early mature type, which indicates that the organic matter of the Domanik sediments has not reached the full maturity characteristic of the peak of oil

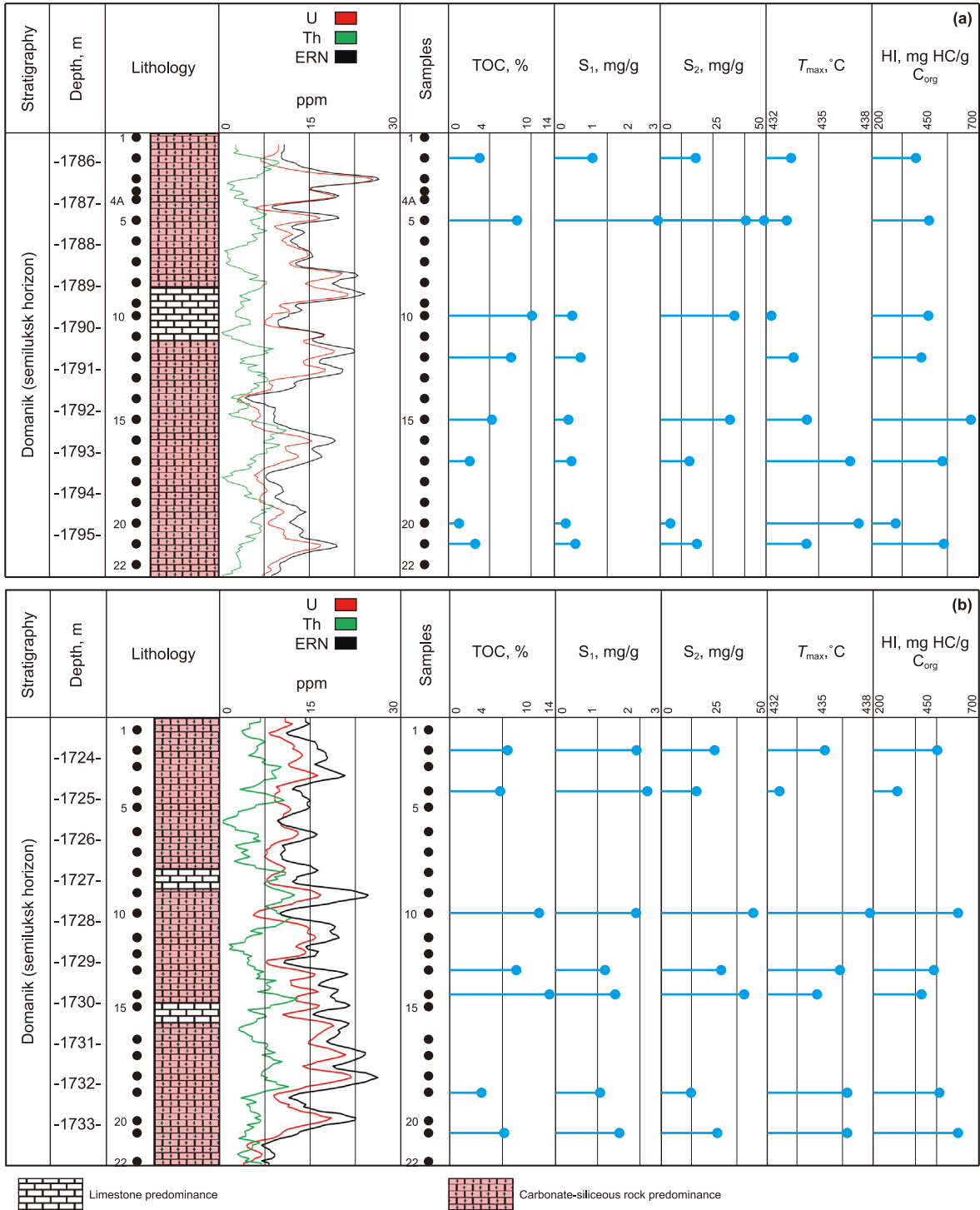


Fig. 8. Plot showing the lithology column of the Domanik sediments (Semiluksk horizon) in Well 1 (a) and Well 2 (b) with the results of pyrolytic studies. U: Uranium; Th: Thorium; ERN: Total radioactivity; TOC: Total organic content. See the wells' location in Fig. 2(a).

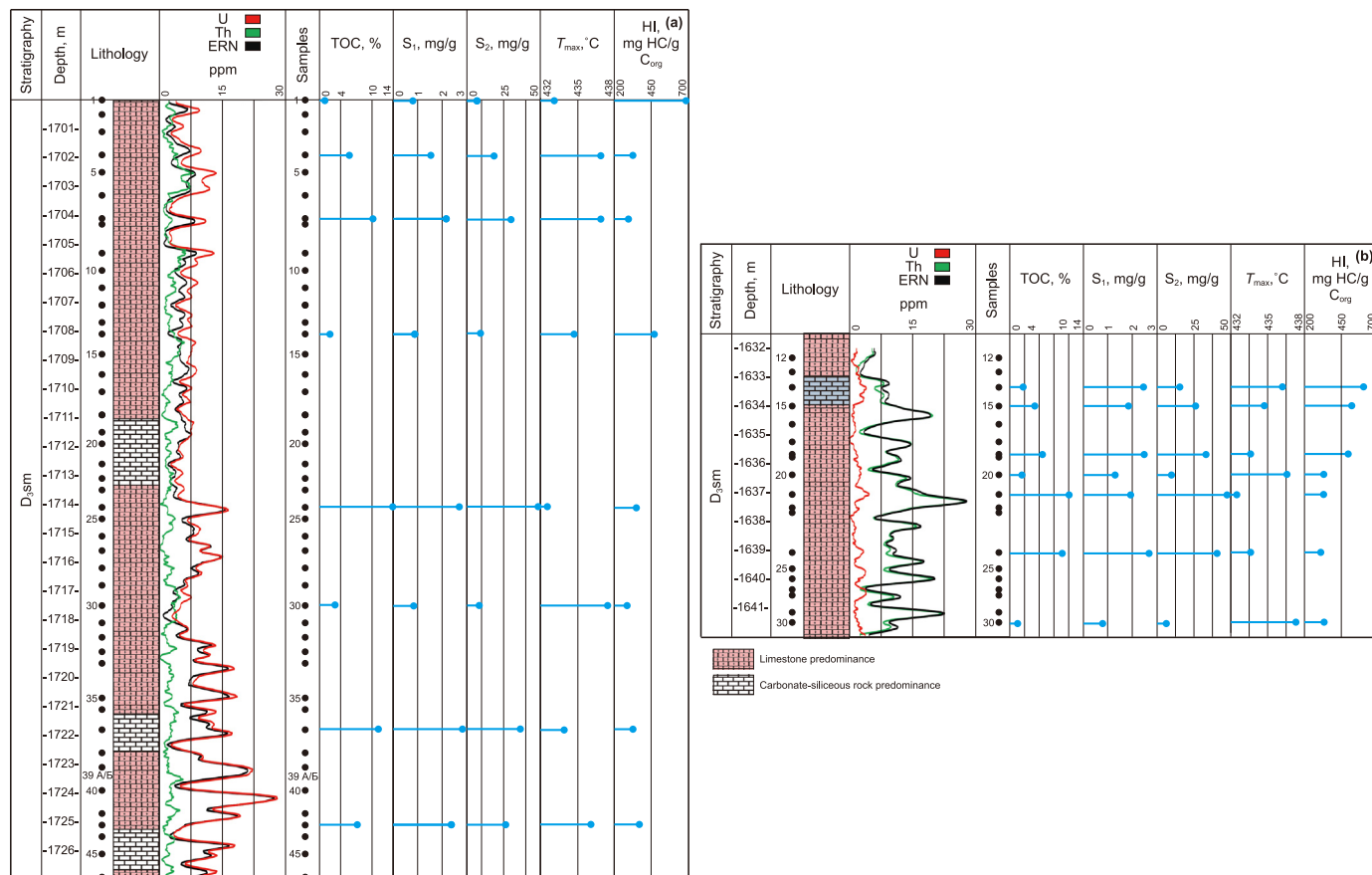


Fig. 9. Plot showing the lithology column of the Domanik sediments (Semiluisk horizon) in Well 3 (a) and Well 4 (b) with the results of pyrolytic studies. U: Uranium; Th: Thorium; ERN: Total radioactivity; TOC: Total organic content. See the wells' location in Fig. 2(a).

generation; that is, the organic matter is not fully mature. This is also indicated by the fact that many samples have a $T_{\max}$ value below 437 °C (Figs. 8 and 9). Thus, analyzing the data obtained as a result of pyrolytic studies of the organic matter of the studied rocks of the Domanik sediments, it can be said that the rocks did not reach the maximum of the oil generation phase, and the degree of maturity of the organic matter on the maturity scale is located within the “immature-early mature” range. The maximum content of organic matter in the carbonate-siliceous rocks is 14%, while the minimum is 1.2%. The average content of organic matter is between 7% and 10%.

5. Discussion

5.1. Genesis of the quartz in Domanik sediments

To understand the genesis of quartz in the Domanik sediments, it is important to consider the results given in Tables 4 and 5, which show that quartz and calcite form a strong negative bond. This indicates different geochemical and ecological conditions for the deposition of calcite and quartz in the Domanik sediments. Another important fact is the anomalous thermal behavior of the quartz, which was detected during the synchronous thermal analysis where on the DSC curve of the studied samples, the endothermic effect of the quartz at 573 °C was not detected, which indicates the anomalous nature of its thermophysical properties. Such quartz differs from the quartz of clastic rocks (Fig. 6(b)) and corresponds to the quartz of technical jasper (Fig. 6(c)), which initially had a hydrothermal-sedimentary genesis. At the same time, in terms of

thermophysical properties, quartz from the Domanik sediments is not only comparable to quartz samples from hydrothermal genesis.

The absence of the endothermic effect of the quartz during thermal studies was previously established on samples of biogenic cherts. Quartz in such rocks is represented by authigenic chalcedony (Yuldashbayeva et al., 2018). This is confirmed in another work, which shows the absence of an endothermic effect in crystalline SiO₂, which has a large structure defect (Smykatz-Kloss, Klinker, 1997). In our opinion, quartz in the Domanik sediments (Semiluisk horizon), which is distinguished by a high degree of structural defects, was formed during sediment genesis in the form of amorphous phases, subsequently turning into chalcedony during catagenesis. This is also confirmed by SEM analyses, where quartz is also not found in the form of clastic grains and is characterized by isometric and not-faceted crystals, resembling flakes, and crystals up to 5 μm in size. It is possible that quartz of both biogenic and hydrothermal genesis is present in Domanikites sediments. This is indicated by the lack of correlation between SiO₂ and TOC ($R^2 = 0.048$), which is often found in black shales (He et al., 2017).

5.2. Mechanism for increasing bioproductivity

5.2.1. Upwelling action

According to one of the hypotheses, the main factor that increases the bioproductivity of the Domanik sea is the periodic influx of large masses of nutrients into the photic zone due to the implementation of enhanced vertical circulation of water masses caused by meteorological factors (seasonal upwelling) (Strakhov, 1960; Rostovtseva and Han, 2017). Currently, several geochemical

modules have been developed that indicate the effect of upwelling on the sediment genesis of the Domanik sediments. One of them is the ratio of Cd/Mo and $\text{Co} \times \text{Mn}$ (Sweere et al., 2016).

It is believed that Cd is an element that enters the sediment together with organic matter during the death of plankton (Haraldsson et al., 1991). Thus, in recent sediments formed in hydrographically limited basins with low primary bioproductivity, e.g., the Black Sea, the Cd content is significantly lower than in sediments formed in water bodies in which upwelling processes are implemented (Conway and John, 2015). Mo, in turn, is considered an element that exhibits conservative behavior in the water column and is able to enter the sediment due to the formation of sulphides in hydrographically limited water bodies (Little et al., 2015).

Co and Mn enrichment in recent marine sediments is controlled by detrital input and authigenic enrichment (Lyons et al., 2003). Modern upwelling zones show low abundances of Co and Mn. Firstly, due to the fact that in upwelling zones, the supply of nutrients is carried out along with deep waters, which are usually devoid of Co and Mn. Secondly, due to the far distance of the basins from the coastline and the minimal contribution of river runoff to the basin. Thirdly, due to the implementation of the “Mn-conveyor belt” (Brumsack, 2006), during which the solubility of Mn changes depending on redox conditions, the mobilized Mn is carried into the ocean in open sea basins. Cd/Mo ratios above 0.1 are typical for upwelling conditions and below 0.1 for hydrographically limited conditions. While the value of the product $\text{Co} \times \text{Mn}$ above 0.4 indicates the limitation of the marine basin (Fig. 10(a) and (b)).

For a better understanding of the conditions for the formation of Domanik sediments, the graphs presented in Figs. 11 and 12 were constructed. According to the reconstruction carried out, the Domanik sea was a marine basin with variable hydrological conditions. It was implemented as seasonal upwelling processes that increase the primary bioproductivity in the paleobasin and as processes leading to the stratification of the water column. Compared to the modern marine basins, the Domanik sea occupies an intermediate position between the Namibian Margin (East Atlantic) and the Cariaco Basin (Gulf of Cariaco in Venezuela) (Sweere et al., 2016).

5.2.2. Hydrothermal activity

Hydrothermal activity is also considered one of the possible factors that increase the bioproductivity in the Domanik basin (Liang et al., 2020; Gottich and Pisotsky, 2017). According to some

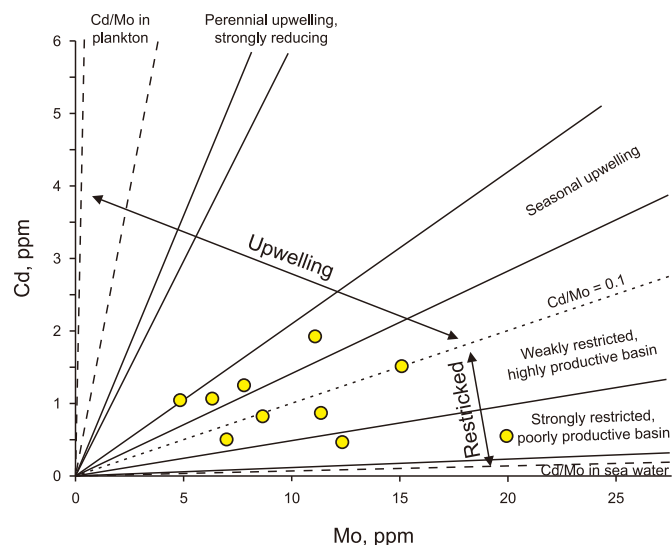


Fig. 11. Cd behavior and Mo in the studied samples from the Domanik sediments of the Volga-Ural petroleum province (Sweere et al., 2016).

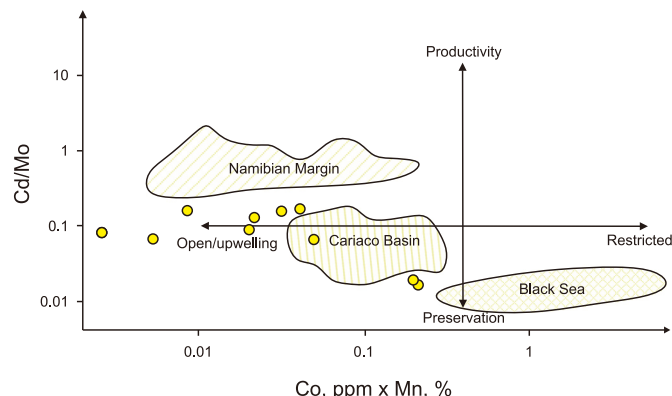


Fig. 12. Behavior of Cd/Mo and $\text{Co} \times \text{Mn}$ in the studied samples from the Domanik sediments of the Volga-Ural petroleum province with examples of other marine basins (Sweere et al., 2016).

studies, it can increase the biological activity by almost four times

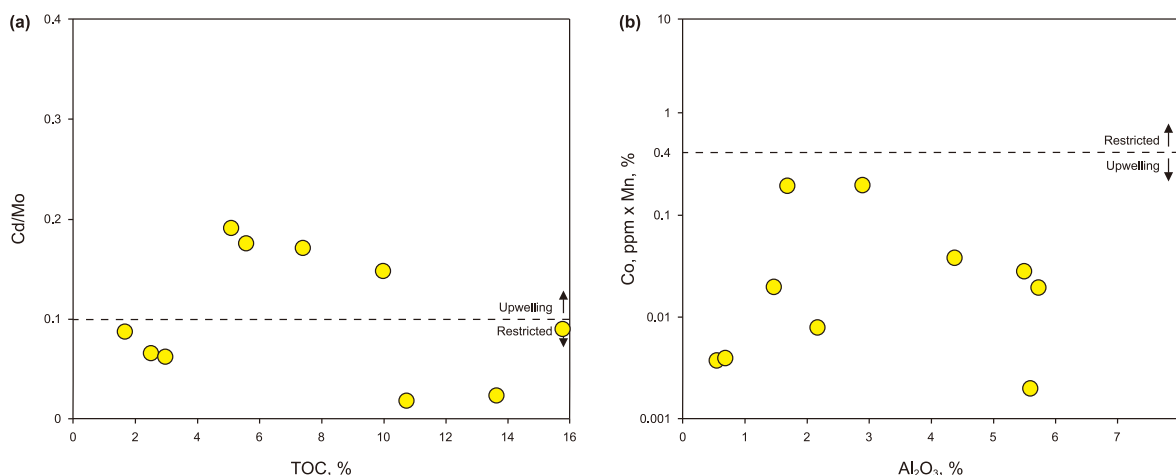


Fig. 10. Graphs of Cd/Mo-TOC and $\text{Co} \times \text{Mn}$ - Al_2O_3 constructed of the studied samples from the Domanik sediments of the Volga-Ural petroleum province (Sweere et al., 2016).

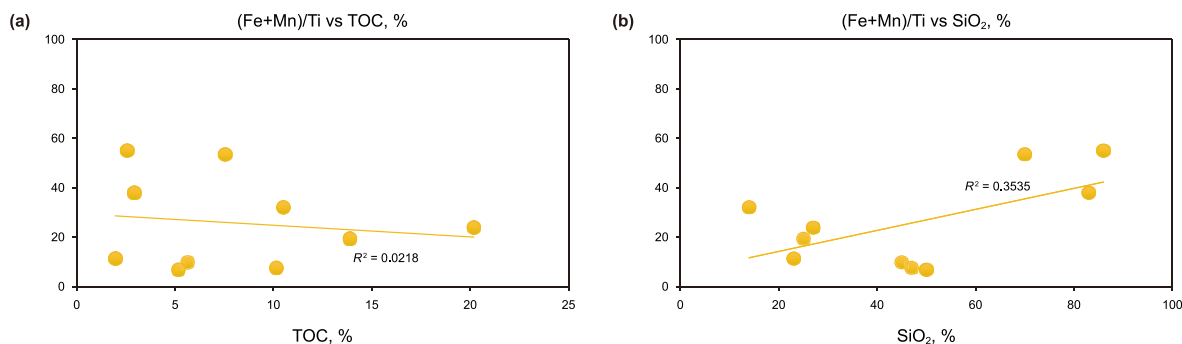


Fig. 13. Graphs $(\text{Fe} + \text{Mn})/\text{Ti}$ vs. TOC%, and $(\text{Fe} + \text{Mn})/\text{Ti}$ vs. SiO_2 for the studied samples from the Domanik sediments of the Volga-Ural petroleum province.

the normal productivity of the ocean surface (Awan et al., 2020). There is several indirect evidences indicating the existence of hydrothermal activity in the marine basin in the Devonian and, later, the disposition of the Domanik sediments starting from the Semiluksk time. Thus, some works document signs of Devonian volcanism and rifting on the territory of the East European platform (Staroverov et al., 2012; Yutkina et al., 2017; Shein et al., 2020). Other researchers have studied the Kama-Kinel trough system, which largely determined the zones of Domanik sedimentation in post-Semiluksk time (Morozov et al., 2022), which is recognized as a tectonic formation, the evolution of which occurred with the formation of numerous faults (Gorozhanina et al., 2019).

According to some studies, the presence of exhalation components in sediments can be estimated from the geochemical modulus $(\text{Fe} + \text{Mn})/\text{Ti}$ (Strakhov, 1976). Iron and manganese in this case are exhalation components, while titanium is terrigenous. If the modulus exceeds 25 units, then the presence of products of volcanic emanations in sediments can be assumed. At present, the modulus of the Red Sea rift exceeds 1000 units (Maslov, 2006). According to the results of ICP-MS for the studied 10 samples, the modulus values $(\text{Fe} + \text{Mn})/\text{Ti}$ vary from 6.7 to 54 units, which may indicate a periodic effect of underwater volcanic emanations on genesis of the Domanik sediments. Fig. 13 shows the plots of $(\text{Fe} + \text{Mn})/\text{Ti}$ -TOC and SiO_2 .

The graph $(\text{Fe} + \text{Mn})/\text{Ti}$ vs. TOC shows that 40% of the studied samples were formed under the influence of hydrothermal activity. At the same time, the intensity of hydrothermal activity did not

affect the amount of organic matter contained in Domanik sediments ($R^2 = 0.02$). Quite differently, volcanic emissions affected the silica content in the sedimentation basin. On the graph $(\text{Fe} + \text{Mn})/\text{Ti}$ versus SiO_2 , a direct dependence is found ($R^2 = 0.35$), i.e., with an increase in the amount of exhalation components in the sediment, the content of silica increases. In fact, this indicates the introduction of silica along with hydrothermal fluids.

The influence of hydrothermal activity can also be estimated from the triangular diagrams Ni, Zn, Co, and Fe, Mn, $(\text{Ni} + \text{Co} + \text{Cu}) \times 10$ (Choi and Hariya, 1992) (Fig. 14(a) and (b)). In the first diagram, the points fell into the area of hydrothermal deposits, while in the second diagram, the points mainly characterize the absence of the influence of hydrotherms on the sedimentogenesis of Domanik. This may be due to the features of the objects on which the diagram data was developed.

According to some studies, a number of these elements can be introduced into the sedimentation basin together with hydrothermal flows (German et al., 1991; Douville et al., 2002; Liu et al., 2019). Thus, hydrothermal activity had a significant impact on genesis of the Domanik sediments of the Semiluksk horizon: hydrothermal emanations introduced silica into the sedimentation basin and increased bioproductivity in the paleobasin. At the same time, the intensity of volcanic emanations did not determine the enrichment of sediments with organic matter, and its content in the rocks was controlled by other factors.

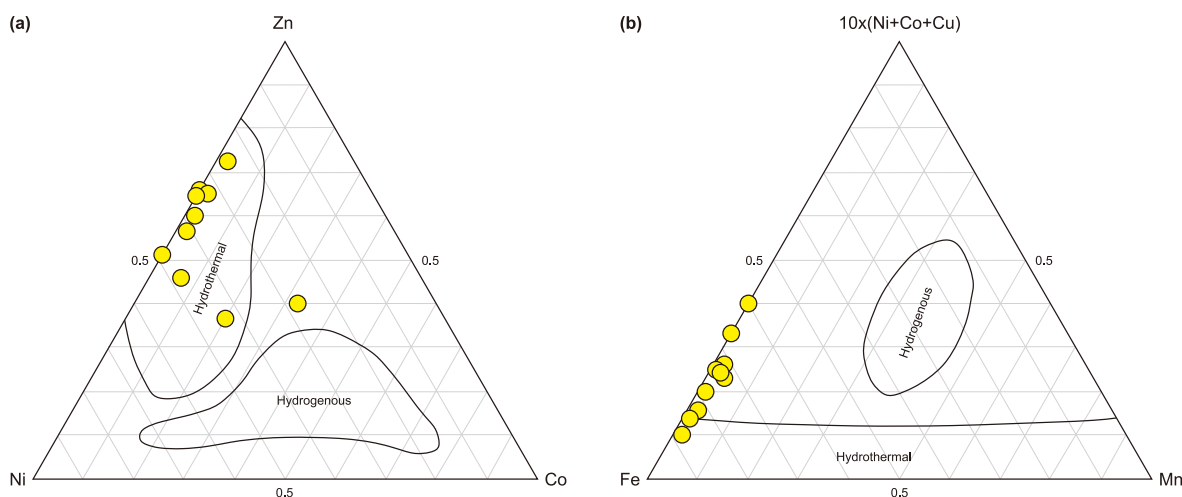


Fig. 14. A plate showing: (a) Triangular Zn-Ni-Co and (b) $10 \times (\text{Ni} + \text{Co} + \text{Cu})$ -Fe-Mn diagrams for the studied samples from the Domanik sediments of the Volga-Ural petroleum province.

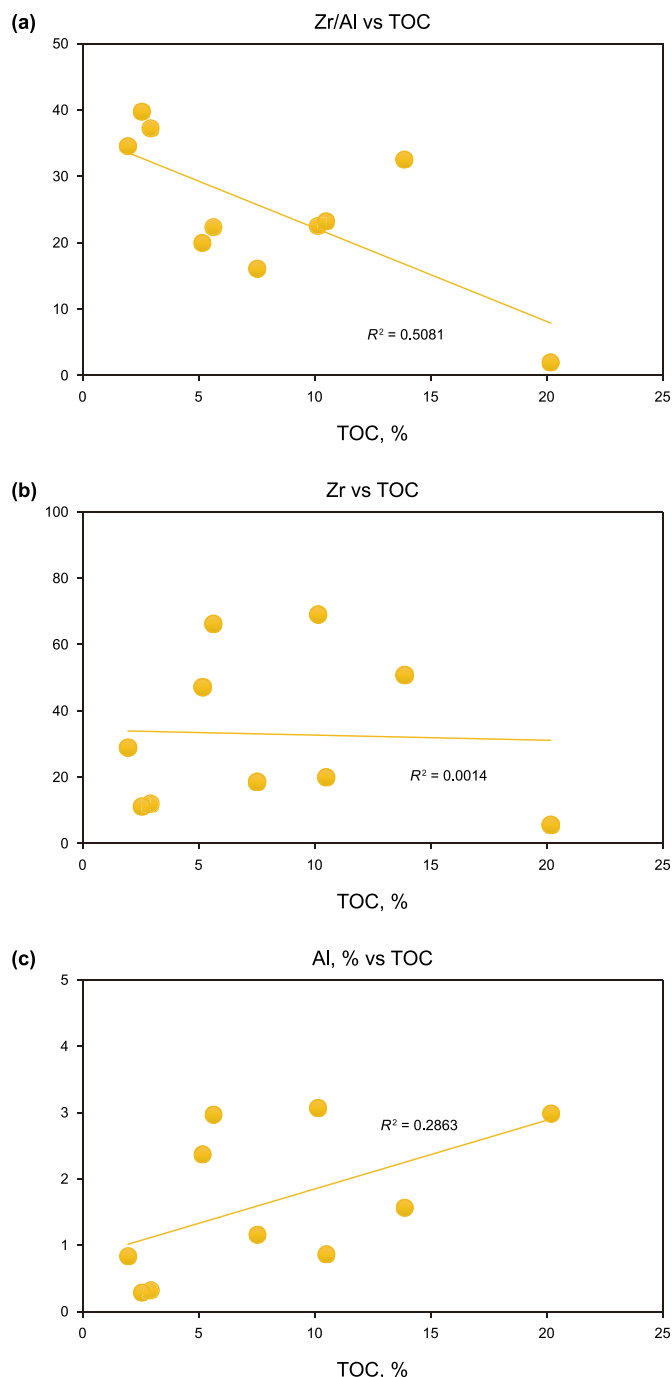


Fig. 15. Graphs showing: (a) Zr/Al vs. TOC %, (b) Zr (ppm) vs. TOC %, and (c) Al (%) vs. TOC % for the studied samples from the Domanik of the Volga-Ural petroleum province.

5.2.3. Volcanic activity

According to many researchers, volcanic activity often causes an increase in bioproductivity in the paleobasin and largely contributes to the formation of the Domanik siliceous rocks, as well as determining the nature of the saturation of rocks with organic matter (Du et al., 2021; Shen et al., 2019; Yang et al., 2021). Ash layers up to 3 cm thick were previously observed in the Domanik sediments (Shakirov et al., 2022). Moreover, according to Shakirov, the introduction of volcanic ash into the sedimentation basin is the determining factor in the accumulation of silica and organic matter

in the studied Domanik sediments (Maksimova, 1970).

Using the Zr/Al ratio, it is possible to evaluate the effect of volcanic ash on the sediment genesis of the lacustrine shales (Pang et al., 2022). Zr in this case is considered a weathering-resistant element that could be brought both by river flows from the continent during the weathering of igneous rocks and soon after a volcanic eruption, together with the ash material (Yang et al., 2022). Al is considered a terrigenous component brought along with aluminosilicates, for example, clays, which are smaller than zircon crystals and, therefore, can be transported much farther from the continent (Racki et al., 2002; Calvert and Pedersen, 2007).

According to modern concepts, volcanic ash is rich in micro-nutrients that are nutritious for plankton (He et al., 2016; Liu et al., 2007). For this reason, for some black shales complexes affected by volcanic activity, a direct positive Zr/Al-TOC relationship is found (Pang et al., 2022). For the studied Domanik samples, the Zr/Al ratio varied in the range from 1.9 to 39.73 ppm/w.t.%, with an average value of 24.8 ppm/w.t.%. At the same time, proxy Zr/Al forms a strong negative bond with TOC ($R^2 = 0.5$), and Zr has no bond with TOC ($R^2 = 0.001$). At the same time, Al has a moderately positive relationship with TOC ($R^2 = 0.28$; Fig. 15). This can be explained by the lack of influence volcanic activity has on bioproductivity of the paleobasin and the addition of Al together with terrigenous components. Thus, we recognize the effect of volcanic processes and the introduction of ash material into the Domanik sea since this is primarily confirmed by the actual material (Khayuzkin et al., 2021). However, apparently, the ash did not increase the primary bioproductivity of the paleobasin, and its influence on genesis of the Domanik sediments of the Semiluksk horizon and enrichment of the rocks with organic matter should be denied or recognized as strictly limited.

5.3. Redox conditions

Analysis of Mo and U behavior with the construction of cross-plots of Mo/U covariation is used to reconstruct the paleoecological environment of lakes and sea basins (Rico et al., 2019; Schobben et al., 2020). Mo and U crossplot (Fig. 16(b)) can have different geochemical behaviors that depend on redox conditions and processes in marine depositional systems (Algeo and Tribouillard, 2009). The resulting ratios Mo:U $\sim 0.3 \times$ SW with sediments average enrichment factors (EF, see chapter 3.2.10) may indicate the existence of anoxic conditions in the sedimentation basin, while most samples fall in the region Mo:U $\sim 1 \times$ SW and $\sim 3 \times$ SW, which at high EF indicates euxinic redox conditions in the Domanik sea (Tribouillard et al., 2012; Fig. 16(a)). At the same time, the behavior and nature of the resulting trend allow us to conclude that Domanikites accumulated in the unrestricted marine.

Another way to assess redox conditions in the paleobasin is the ratios of U and Th, as well as V and Cr (Zhao et al., 2016; Liu et al., 2019, 2022). U/Th ratios < 1.25 and V/Cr < 2.0 indicate oxygen conditions, while U/Th ≥ 1.25 and V/Cr > 4.25 suggest the existence of anoxic environments in the sedimentation basin (Nath et al., 1997; He et al., 2019). In the samples from the Domanik sediments, the U/Th ratios varied from 2.8 to 27 units, which indicates the existence of anoxic conditions in the sedimentation basin. V/Cr values varied from 1.09 to 23 units, which confirms those obtained using U/Th proxy results. U/Th and V/Cr form a weak positive relationship with the content of organic matter in the Domanik of the Semiluksk horizon (Fig. 17).

Apparently, redox conditions influenced the enrichment of domanikites with organic matter. At the same time, according to the obtained relationship within U/Th, V/Cr and content of organic matter, redox conditions did not control the enrichment of organic matter.

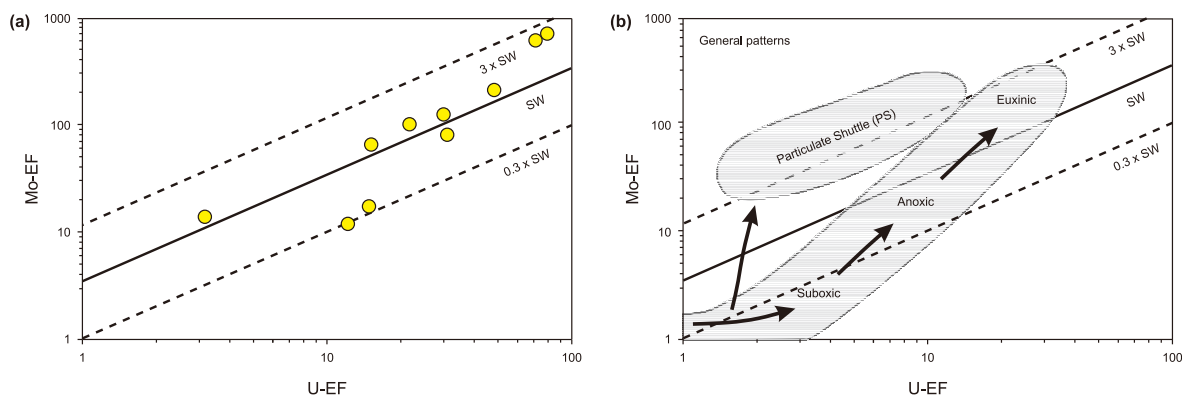


Fig. 16. Crossplots of Mo/U covariations: (a) Samples of Domanik siliceous rocks; (b) General patterns of U–EF vs. Mo–EF covariation in modern marine environments (Tribouillard et al., 2012).

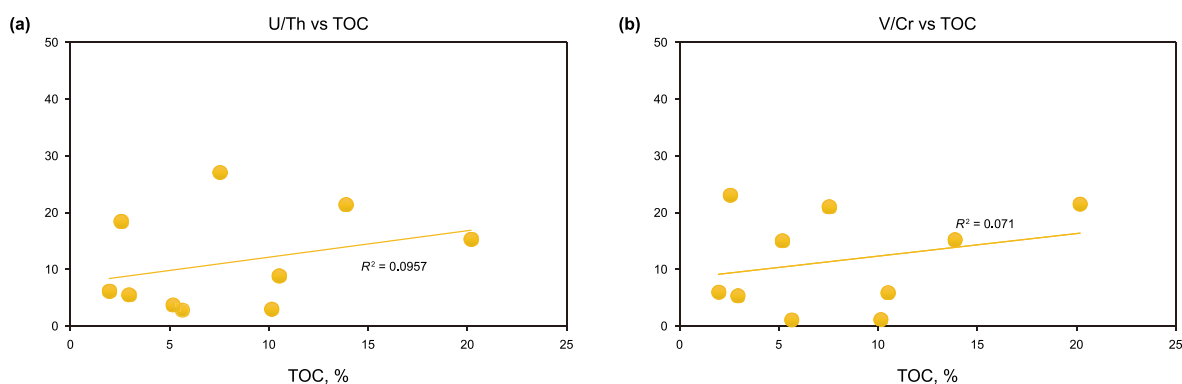


Fig. 17. U/Th vs. TOC and V/Cr vs. TOC diagrams of the studied samples from the Domanik sediments of the Volga-Ural petroleum province.

5.4. Contribution of terrigenous flows

According to the literature data as well as paleogeographic reconstructions, Domanik sediments accumulated along the palaeoequator line within a relatively deep-sea shelf, and the zone of accumulation of oil source sediments was far from the coastline (Kazmin and Natapov, 1998; Liang et al., 2020). The proxy Ti/Al is used to estimate the amount of clastic material in the basin and the transport distance (Murphy et al., 2000; Rimmer, 2004). For the studied samples from the Domanik sediments, it varied from 0.01 to 0.093. At the same time, Ti/Al shows a strong negative relationship with TOC ($R^2 = 0.33$), while Ti-TOC does not form a significant relationship ($R^2 = 0.01$).

Based on our interpretations, it is believed that the contribution of the terrigenous flows to genesis of the Domanik sediments was very limited. This is confirmed by the results of analytical studies, which showed that the detrital mineral grains are not detected under the electronic microscope, and the mica content calculated using XRD analysis rarely exceeds 4%. Also, this is consistent with earlier published works (Stupakova et al., 2015a,b; Kolchugin et al., 2018).

5.5. Conditions of the Domanik sediments formation

According to our interpretations and the available literature (Liang et al., 2015), the Domanikites sediments settled in a semi-limited anoxic basin that occasionally turned euxinic during the Semiluksk period. This was made possible by transgression, which increased the water-sea depth to 200–300 m (Liang et al., 2015). The sea water was characterized by variable hydrodynamic

conditions, which could be determined by the seasonal nature of upwelling, which, in turn, contributed to bioproductivity. Additionally, during the upwelling in the Domanik sea, water mixing occurred, which led to a moderate enrichment of bottom waters with oxygen, as a result of which organic matter was not completely buried. At the same time, when there was no upwelling, the stratification of the water column intensified, which led to the appearance of euxinic conditions and increased burial of organic matter.

Anoxic conditions in the Domanik sea contributed to the enrichment of sediment with organic matter, but hydrothermal activity should be recognized as the main factor that determined the sedimentogenesis of Domanikites. Hydrotherms flowing directly into the Domanik sea or beyond its boundaries introduced exhalative components into the sediment, which were found in large quantities in carbonate-siliceous rocks enriched in organic matter. In addition, along with hydrothermal solutions, SiO_2 , which, in addition to biogenic extraction, was deposited chemogenically from supersaturated sea water, were apparently introduced.

It is possible that the processes of hydrothermal outpouring were simultaneously accompanied by volcanic activity, traces of which are found in the Domanik cores (Maksimova, 1970; Khayuzkin et al., 2021; Shakirov et al., 2022). This is indicated by a positive relationship between the content of exhalative NiO, CuO, ZnO, and MnO and components that could be introduced aurally, together with volcanic ash: ZrO_2 and TiO_2 . These factors, in our opinion, determined the environmental and geochemical conditions in the Domanik sea (Fig. 18). Thus, the periodic supply of hydrothermal fluids, together with the hydrodynamic regime of the sea as well as redox conditions, determined the alternation of

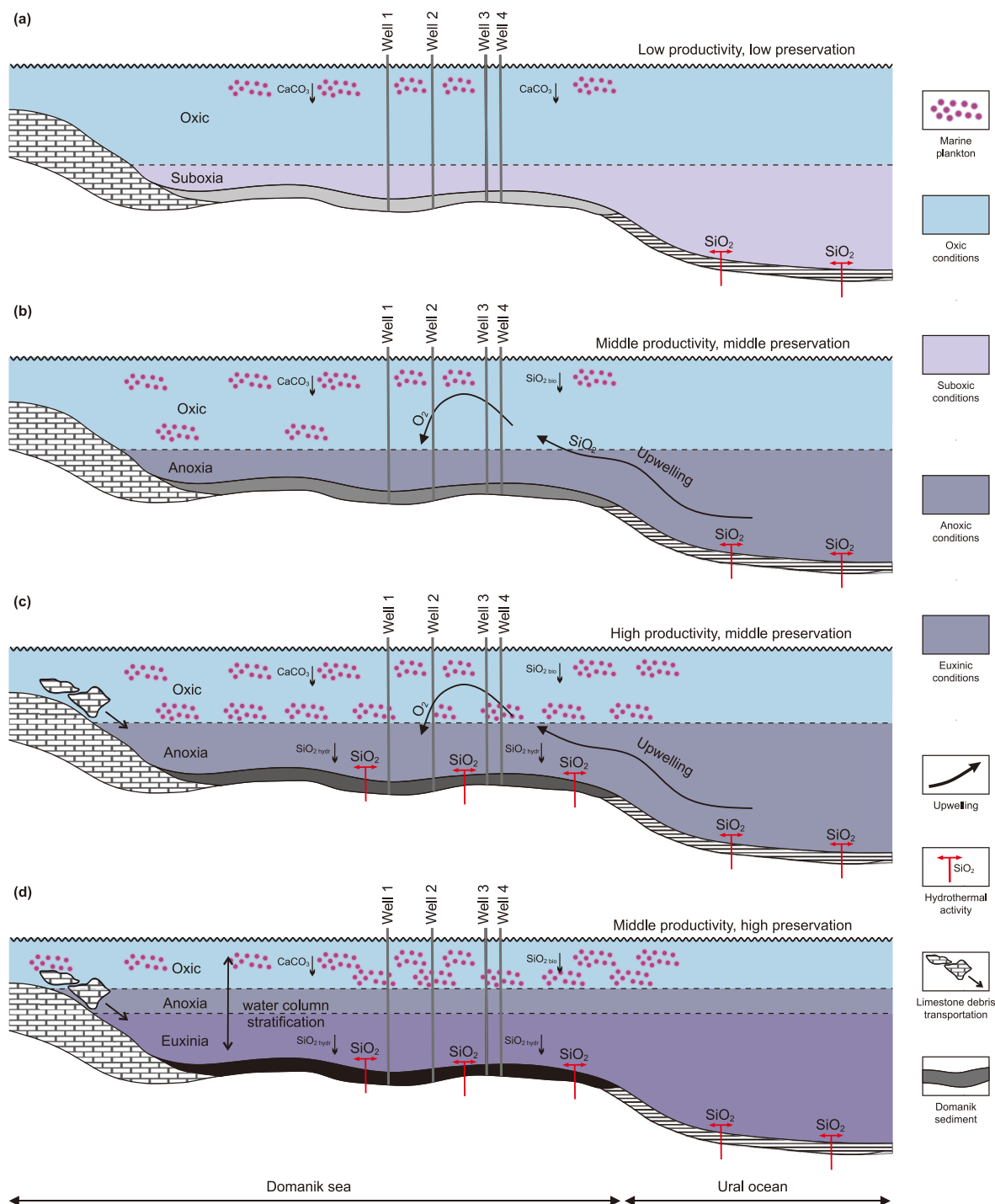


Fig. 18. Scheme of the Domanik sediments genesis showing: **(a)** Model of the Domanik sea without upwelling processes and hydrothermal activity; the sea is characterized by low productivity and suboxic conditions; such samples were not identified in this study, but we assume the presence of such conditions; **(b)** Model of the Domanik sea with upwelling processes that increase the basin productivity, which, in turn, leads to anoxia conditions in the sedimentation basin; water mixing within the basin does not allow formation of the stratification of the water column and euxinic conditions; **(c)** Model of the Domanik Sea during natural disasters (earthquakes and volcanic activity), accompanied by upwelling and hydrothermal activity directly in the Domanik sea, which greatly increase the productivity of the basin; mixing of waters within the basin does not allow formation of the stratification of the water column; **(d)** Model of the Domanik sea during natural disasters (earthquakes and volcanic activity) with hydrothermal activity directly in the Domanik sea, which moderately increases the productivity of the sedimentation basin without upwelling processes. The absence of hydrodynamics contributes to the stratification of the water column and the formation of euxinic conditions in the bottom part of the basin.

carbonate and carbonate-siliceous rocks, the thickness of which in the core ranges from 0.1 mm to 0.5 m, as well as the degree of organic matter enrichment of the rocks.

We believe that carbonate breccias, constantly present in the

studied sections, may be evidence of periodic natural disasters similar to earthquakes that accompanied volcanic activity and the outpouring of hydrotherms. The cement in such breccias is always carbonate-siliceous material enriched in organic matter. The

formation of such formations is explained by the manifestation of slope processes, which manifested themselves during natural disasters in the form of the separation of lithified limestones and their transfer into carbonate-siliceous sediment under the influence of gravitational forces. Evidence of slope processes is “the presence of interlayers of sedimentary breccias, where intraclasts are represented by both acute-angled and smoothed fragments of limestone. Some of these layers are saturated with fragments of shells of bivalves, crinoids, brachiopods, gastropods, and tentaculites” (Shardanova et al., 2017).

According to some works, the manifestation of slope processes in the Domanik Sea began at the beginning of the Semiluki time, due to the spread of condensed sedimentation from east to west (Tikhomirov, 1995), as a result of which a geomorphological step was formed, which led to the dismemberment of the seabed. In addition, in our opinion, the dissection of the seabed could appear due to a significantly higher rate of accumulation and lithification of carbonates relative to carbonate-siliceous rocks enriched in organic matter (Kuznetsov, 1992).

6. Conclusions

The detailed integrated study of the Domanik sediment using the geochemical and sedimentology investigations resulted in the following conclusions.

1. Due to variations in the geochemical and environmental conditions in the sedimentation basin during sediment formation, the carbonate and carbonate-siliceous rocks enriched in organic matter form a cyclicity in the Domanik sediment section. The carbonate breccias lithotype is uncommon in the Domanik sediment section.
2. By analogy with recent marine basins, the Domanik sea is located between the Namibian Margin (East Atlantic) and the Cariaco Basin (Gulf of Cariaco in Venezuela). The increasing amount of organic matter, carbonate material, and free silica in the Domanik formation conditions of high-carbon strata might be the result of hydrotherms or volcanogenic products in the late Devonian. The seasonal upwelling and hydrothermal activity, together with the periodic inflow of hydrothermal fluids, including free silica, resulted in the flourishing of biota and the buildup of sapropelic organic materials. In addition, anoxic and euxinic conditions existed in the Domanik Sea, which influenced organic matter burial in the sediments.
3. Geochemical studies indicate that the Domanik (Semiluksk horizon) has high-carbon deposits. The well-preserved conditions and strong plaeoproductivity of these sediments make them essential for organic carbon enrichment.
4. Based on the available data, the Domanik sediments seem to be the most favorable oil targets in the Volga-Ural petroleum province. However, there are several unclear aspects regarding the reservoirs, such as petrophysical characterization, regional distribution of the reservoir units, diagenesis and its impacts on the reservoir quality, etc.; the relationship between organic matter enrichment and volcanic activity is also a significant research concern.

CRediT authorship contribution statement

Alexey Khayuzkin: Writing – original draft, Methodology, Conceptualization. **Vladimir Morozov:** Supervision, Project administration. **Anton Kolchugin:** Data curation. **Yousef Ibrahim:** Writing – review & editing, Data curation. **Eduard Korolev:** Formal analysis, Conceptualization. **Alexey Eskin:** Formal analysis. **Timur**

Zakirov: Formal analysis, Methodology, Visualization. **Evgeniya Morozova:** Formal analysis. **Nafis Nazimov:** Resources, Funding acquisition. **Flera Gazeeva:** Resources, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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