

Organic Geochemistry of Oxfordian Carbon-rich Sedimentary Rocks of the Russian Plate

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Abstract—The lithology and geochemistry of upper Oxfordian sedimentary rocks enriched in marine organic matter (OM) have been studied. These rocks occur as a persistent unit of Upper Jurassic rocks exposed on the right bank of the Unzha River in the Kostroma district. The OM was investigated in detail in both the carbon-rich rocks and their hosts. It was established that the OMs from the Oxfordian rocks are characterized by a low degree of thermal (catagenetic) maturity and their geochemical signature reflects specific features of synsedimentary and early diagenetic processes. Kerogen in the carbon-rich sedimentary rocks is markedly enriched in S_{org}, and its formation was related to the early diagenetic sulfate reduction (sulfurization of the lipid fraction of the initial OM). The composition of kerogen from the host clay is sharply distinct in many parameters. No derivatives of isorenieratene were revealed in the aromatic fraction of bitumen in the carbon-rich rocks. The Oxfordian carbonaceous rocks are distinguished by slightly enriched in S, Mo, V, and Ni. Anoxic conditions were unstable in the water column during the deposition of carbon-rich sediments (such conditions were probably episodic). The C_{org}-rich unit formed due to a short-term abrupt increase in the productivity of phytoplankton related to eutrophication of water, probably, as a result of the recycling and redistribution of biophile elements.

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INTRODUCTION

Environments favorable for the accumulation of autochthonous OM in sediments appeared repeatedly in Late Jurassic–Early Cretaceous marine basins of the Russian Plate. The Upper Jurassic interval includes the well-known sequence of intercalating clays and oil shales (C_{org} up to 10n%) pertaining to the *Dorsoplanites panderi* ammonite zone. The present-day occurrences of this sequence makes up a zone extending throughout the eastern Russian Plate from the Caspian Sea to the Barents Sea (Strakhov, 1934; Yavkhuta, 1979; Braduchan et al., 1989). The Lower Cretaceous (lower Aptian) bituminous shale is widespread in the Middle and Lower Volga region (Gavrilov et al., 2002). The lower Valanginian rocks are also known in the northern Russian Plate (Vasil'eva et al., 1989; Lyyurov, 1996).

Results of the sedimentological and paleontological investigations (Strakhov, 1934; Riboulleau et al., 2000; Gavrilov et al., 2002) and the geochemical investigation of OM (Bushnev and Burdel'naya, 2003; Bushnev, 2005) of the middle Volgian and Aptian marine carbon-rich shales at the Russian Plate testify to various levels of C_{org} concentration and different oxygen regimes in bottom waters of the respective basins.

Since Upper Jurassic rocks are characterized by a high level of OM accumulation (up to 15.5 wt % C_{org}), the Oxfordian unit merits special attention. This unit occurs locally in the northwestern Moscow Syncline in the Upper Jurassic sequence that crops out on the right bank of the Unzha River near the town of Makar'ev, Kostroma district (*Stratigrafiya...*, 1972; *Srednii...*, 1989). The sedimentological features and geochemistry of OM from the Oxfordian carbon-rich rocks have not been comprehensively discussed in the literature so far. We studied these rocks in detail in order to reconstruct the oxygen regime and its variation in the course of marine OM accumulation.

EXPERIMENTAL

The **organic carbon** (C_{org}) was determined for the insoluble (in hydrochloric acid) rock residue with an AN-7529 express-analyzer of carbon. Results of the measurements were recalculated to the initial rock composition. Glucose and low-carbon steel were used as standards.

Chloroform-soluble bitumen A (CBA) was extracted from ground rock in a Soxhlet apparatus over 40 h. Elementary sulfur was removed from the extract by the addition of sponge copper to the receiver.

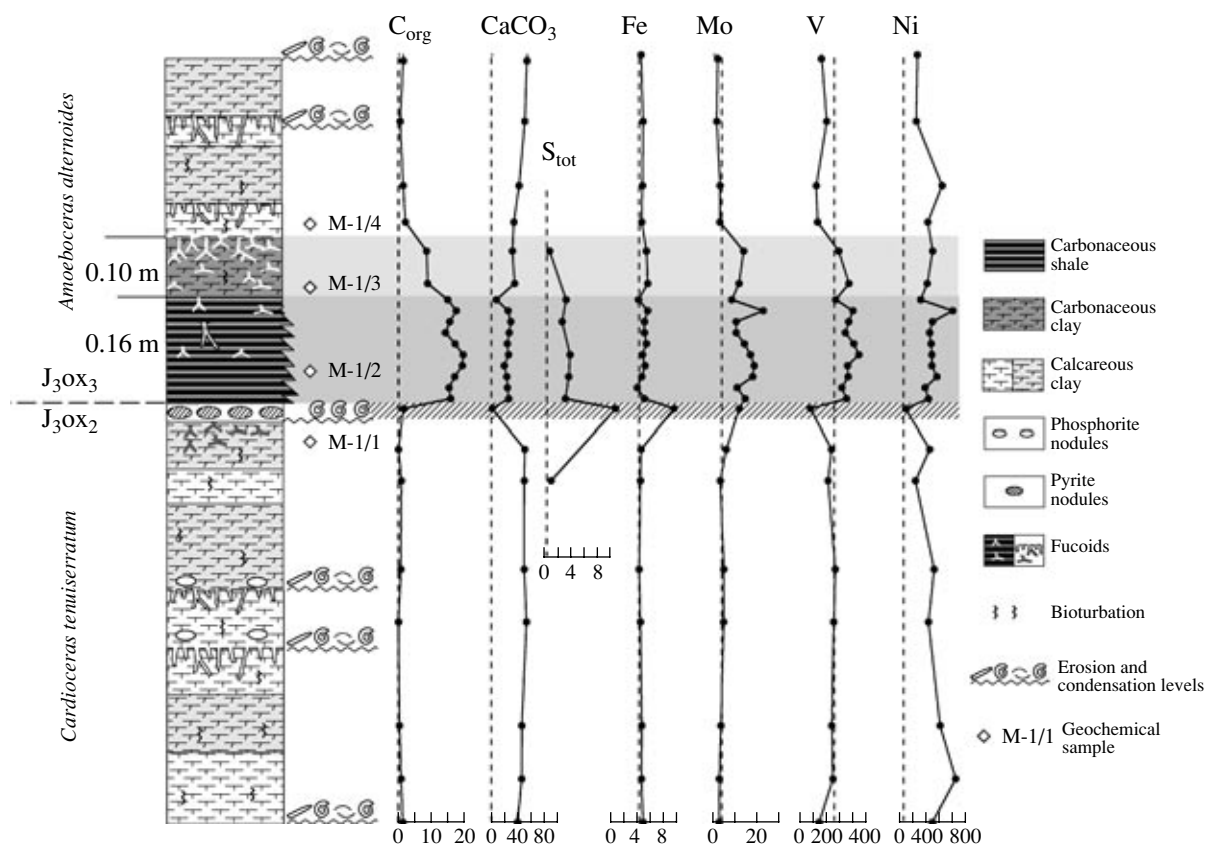


Fig. 1. Structure and geochemical characteristic of the Oxfordian carbon-rich unit. The right bank of the Unzha River near the town of Makar'ev, Kostroma district, Russia. Concentrations of chemical elements are recalculated to the carbonate-free material; dashed lines mark clarke abundances of elements in clayey rocks, after (Turekian and Wedepohl, 1961).

The CBA was divided into fractions by column chromatography. An apolar fraction was obtained by the fractionation of asphaltene-free CBA on Al_2O_3 (F2 is eluted with 10%-dichloromethane in *n*-hexane). Then, the apolar fraction was separated on silica gel into the saturated (F4 eluent *n*-hexane) and aromatic (F5 eluent benzene) fractions. In order to conduct the quantitative analysis, the initial CBA was spiked with two standards: 3-methyl-6,6-dideuteriotriaecosane (passing into F4) and 2-methyl-5-(1',1'-)-dideuteriooctadecyl)-thiophene (passing into F5).

Kerogen was extracted from samples by the method of acidic demineralization with hydrochloric and hydrofluoric acids. Completeness of the removal of mineral constituent was checked on the basis ash content in the kerogen concentrate.

Pyrolysis of kerogen was carried out in a jet quartz reactor at 410°C in nitrogen flow (Bushnev, 2001). Pyrolysates were trapped by chloroform at 0°C.

Fractions of saturated hydrocarbons (F4) were analyzed with the gas chromatography and chromatic mass spectrometry. Fractions of aromatic hydrocarbons (F5) and pyrolysates (P0, P3, and P4) were only analyzed with the chromatic mass spectrometry (Bushnev, 2001; Bushnev and Burdel'naya, 2001).

All analytical works were carried out at the Geological Institute (Moscow). The C_{org} , CO_2 , Fe, Mn, Ti, and P contents were determined in the chemical analytical laboratory; XRD studies, in the laboratory of physical methods for the study of rock-forming minerals (A.L. Sokolova, analyst).

RESULTS AND DISCUSSION

Lithology and Paleontology of the Carbon-Rich Unit

The Upper Jurassic (lower Callovian–lower Kimmeridgian) sequence (~15 m thick), which hosts the OM-rich unit (Fig. 1), crops out on the right bank of the Unzha River near the town of Makar'ev, Kostroma district.

The middle and upper Oxfordian rocks, between which the carbon-rich unit is sandwiched, are similar in lithology and composed of rhythmic-bedded calcareous clays with a significant amount of calcareous nanoplankton remains (37.57–56.70 wt % $CaCO_3$, 0.27–2.37 wt % C_{org}). The rhythmic bedding is expressed in frequent intercalation of dark and light greenish gray clay beds (0.1–0.2 m thick), which differ in contents of the fine-dispersed biogenic carbonate material and OM.

The uneven boundaries of are appreciably deformed by bioturbation. Clays are enriched in various organic remains, mostly represented by fine shelly detritus and intact foraminiferal shells. Numerous ammonite shells, belemnite rostrums, and coarse shelly detritus are concentrated at particular levels that are readily traceable at outcrops. Compact phosphorite nodules are also present. Such enriched levels likely mark the erosion of sediments and the redeposition of the coarsest sedimentary material.

The mineral assemblage in the Oxfordian clay is virtually constant. According to XRD results, the <0.001-mm fraction consists of mixed-layer minerals (smectite–mica with ~30% of micaceous layers), kaolinite, and hydromica (5–10% of expanding layers) as major components, minor amount of chlorite, and quartz and feldspar as admixtures. The Oxfordian clay contains abundant Fe-rich varieties of authigenic fine-dispersed mixed-layer minerals. The bright green color on the fresh fracture of the Oxfordian clay gives way to a pale greenish yellow color in a short time span, probably, due to the presence of Fe⁺² that is rapidly oxidized in air. The nonuniform distribution of authigenic Fe-rich minerals imparts a characteristic yellowish green spotted pattern to the Oxfordian clay that locally passes into distinct secondary-diagenetic bedding.

Based on the foraminiferal assemblage identified in the clays that underlie the carbon-rich unit (0.1 m below the contact), the carbon-rich unit includes the following taxons: *Globigerina oxfordiana* Grig., *Ophthalmidium strumosus* (Gumb.), *Lenticulina brestica* (Mitjan.), *L. hebetata* (Schwag.), *L. spp.*, *Astacolus comptulus* (Schwag.), *A. compressaeformis* (Paalz.), *Trocholina transversari* Paalz, *Ramulina spandeli* Paalz, *Epistomina nemunensis* Grig., *E. uhligi* Mjatl., *E. parastelligera* Hofker, *Paulina fursenkoi* Grig., and *Lingulonodosaria? tuberosa* (Schwag.). As was established previously, this unit corresponds to the upper portion of the middle Oxfordian, i.e., *Cardioceras tenuiserratum* ammonite zone (*Srednii...*, 1989).

The C_{org}-rich rocks are distinguished in the section by the darkest color. They have a sharp even and horizontal contact with the underlying clays. A 3-cm-thick bed with closely spaced pyritized ammonite shells (10–15 cm in diameter) is traceable along this boundary at the Makar'ev outcrop. At present, the surface of shells is replaced with brown-yellow iron hydroxides. This level is akin to the ammonite- and belemnite-rich units that are widespread in the host clay. However, the high concentration of shells suggests that this level marks a prolonged hiatus that predated the OM accumulation in Oxfordian sediments.

The lower portion of the carbonaceous unit (0.16 m) consists of dark brownish gray calcareous C_{org}-rich shales (C_{org} up to 10.40–15.50 wt %). The fine platy parting locally grading into foliation testifies to the uniform horizontal orientation of clay particles and its good prevention from the subsequent bioturbation

(Fig. 2). The bedding planes of carbonaceous shales contain various fossils (intact flattened ammonite shells and large biogenic phosphate detritus with occasional fish skeletons). Small shells of benthic bivalves and sporadic (elongated and nearly horizontal) fucoids are scattered on some bedding planes. Thus, the sedimentological and biotic attributes of the Oxfordian carbon-rich shale indicate that its environmental conditions were unfavorable for the benthic and burrowing fauna, most likely, due to the deficiency in oxygen near the basin bottom. However, the steady anoxic environment hardly existed.

The upper portion of the carbonaceous unit (0.10 m) is intensely bioturbated and composed of dark brownish gray carbonaceous clays with a high C_{org} content (5.70–5.80 wt %), which is lower than that in the underlying shale. The clays contain numerous tracks of *Chondrites* that are well known for their tolerance to the oxygen regime.

The upper clayey part of the unit includes the following foraminifers: *Globigerina oxfordiana* Grig., *Ophthalmidium strumosus* (Gumb.), *Lenticulina brestica* (Mitjan.), *L. hebetata* (Schwag.), *Trocholina transversari* Paalz, *Ramulina spandeli* Paalz, *Epistomina nemunensis* Grig., *E. uhligi* Mjatl., *E. parastelligera* Hofker, and *Lingulonodosaria tuberosa* (Schwag.). As was established previously, the carbonaceous shale and the overlying clay belong to the lower portion of the upper Oxfordian, i.e., *Amoeboceras alternoides* ammonite zone (*Srednii...*, 1989). Our data also support this conclusion.

The lower shaly portion of the unit is mainly composed of the structureless OM (no less than 90% of the OM) that fits colloalginite identified by Ginzburg (1991). Colloalginite is characterized by various hues of yellow and brown colors and is segregated in the calcareous clayey matrix as distinct fragments as long as 0.2 mm. In thin sections cut perpendicular to foliation, the colloalginite fragments appear as small flattened nearly parallel lenses that emphasize the uniform horizontal orientation of clastic components. The thin horizontal bedding caused by the nonuniform distribution of lenticular colloalginite segregations is reflected in variable C_{org} concentrations in samples taken at different levels of the unit. In addition to structureless OM, the shale contains an admixture of fine coalified plant detritus segregated along bedding planes. Remains of spores and pollen of land plants occur sporadically. According to (Hantzpergue et al., 1998), kerogen from the Makar'ev carbonaceous shale corresponds to type II with the hydrogen index (HI) equal to 400–500 mg HC/g TOC, which testifies to the good preservation of OM and its largely marine origin.

The colloalginite content markedly decreases in clays with an elevated C_{org} content from the upper part of the carbonaceous unit. The brown fine-grained OM is densely and uniformly dispersed in the matrix. The isometric colloalginite clots are randomly distributed.

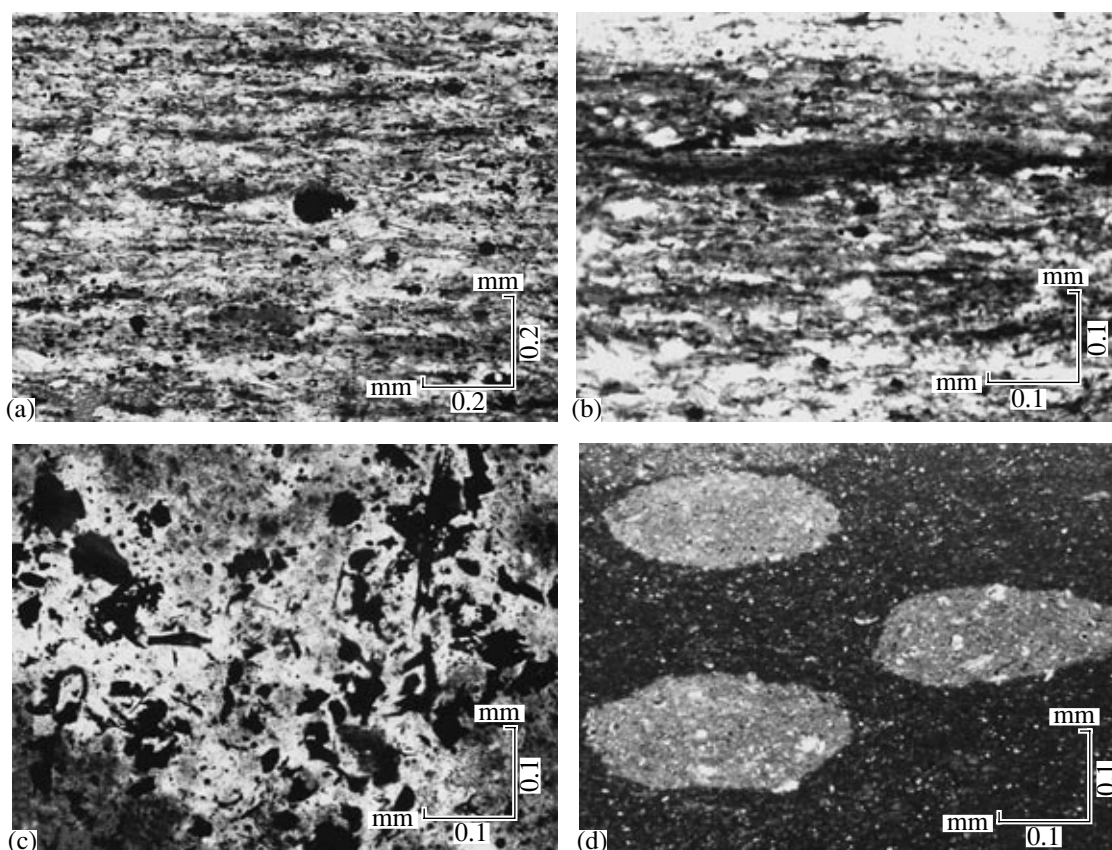


Fig. 2. Microstructures of rocks from the Oxfordian carbon-rich unit. (a) Fine lamination of carbon-rich shale with parallel-horizonal arrangement of fine lenticular laminae of OM (colloalginite); (b) fine lenticular segregations of colloalginite in carbon-rich shale; (c) clusters of fusainized plant detritus on bedding planes of carbon-rich shales; (d) homogeneous (without distinct lamination) microstructure of OM-rich clay from the Oxfordian carbon-rich units. Fucoids are light-colored.

These features show that the marine OM was intensely transformed after its incorporation into clays.

Figure 1 shows that the Oxfordian shale with marine OM is enriched in S (1.82–2.84 wt %), Ni (280–590 ppm), V (250–330 ppm), and Mo (39.9–60.8 ppm). Concentrations of these elements are appreciably higher than their clarkite contents in clayey rocks (Turekian and Wedepohl, 1961) and average concentrations in the host calcareous clayey sediments.

The enrichment in S is not accompanied by a marked variation in the Fe content (3.63–4.22 wt %), which is close to that in the host clay (3.60–4.36 wt %) and the average content of 4.72 wt % in clayey rocks (Turekian and Wedepohl, 1961). Higher concentration of Mo and V (relative to the clarkite level) is a specific feature of the autochthonous marine OM-rich sediments. This is commonly attributed to low solubility of compounds of reduced species of these elements in environments with a considerable deficiency in oxygen.

Elevated Ni concentrations (relative to the clarkite level) is a characteristic feature of Upper Jurassic calcareous-clayey rocks of the studied region as a whole. Concentration of this element in shales is probably related to its adsorption on organic particles and the

subsequent redistribution during early diagenetic processes in the presence of reactive OM.

We compared geochemical parameters of the Oxfordian carbon-rich sediments with the similar (in terms of age and regional setting) middle Volgian oil shales of *Dorsoplanites panderi* ammonite zone near the Settlement of Ivkino ~25 km north of the town of Makar'ev (Shchepetova, 2005) and the early Aptian bituminous shale of the Middle Volga region (Gavrilov et al., 2002). The C_{org} content is 5–27% in the Volgian oil shale and is similar or slightly lower in the Aptian shale (4–9%). However, the Aptian shale is characterized by a wider spectrum of chemical elements and significantly higher S, Mo, and V contents. It is known that these elements are fixed in sediments most readily in anoxic (hydrosulfuric) environments of marine basins. However, such a mechanism was not realized in the Oxfordian basin in full measure.

Paleogeographic Setting in the Studied Part of the Oxfordian Basin

According to the paleogeographic reconstructions (Gerasimov, 1962; Sazonova and Sazonov, 1967;

Sahagian et al., 1996), Late Jurassic marine basins of the Russian Plate were largely shallow-water structures (no deeper than 50–200 m). Generally, they occupied the eastern part of the plate that represents the submeridional zone of the main Mesozoic trough related to the merger of three large (Pechora, East Russian, and Caspian) tectonic depressions. The strait-shaped configuration of the Late Jurassic seas facilitated their links with Mesozoic oceans (Tethys and Boreal Atlantic). However, the transgressive–regressive regime was unstable because of an intermittent character of these links. In this regard, the Unzha region was characterized by the least stable sedimentation regime, because this region was subjected to the influence of both northern and southern oceanic water masses owing to its location in the central Russian Plate.

Continental conditions in the Late Jurassic existed only in restricted areas of marginal zones of the Russian Plate, where the subtropical variable-humid climate fostered chemical weathering (Yasamanov, 1978).

The circumstances mentioned above were responsible for a complex and unstable water circulation system in Late Jurassic seas of the central Russian Plate and a relatively high background level of their eutrophication. This is expressed in the abundance of diverse fossils and biogenic–authigenic neogenic minerals (phosphorites, glauconite, and others). The presence of terrigenous admixture resulted in the prevalence of the biogenic–terrigenous type of sedimentation that is favorable for imprints of diverse biotic changes on the composition of sediments.

The lithological and paleontological characteristics of the Oxfordian sedimentary rocks in the Unzha area show that the specific features listed above are inherent to the Oxfordian basin in full measure. Accumulation of autochthonous OM and its retention in sediments of this basin was promoted by the regime of cyclic biogenic–terrigenous sedimentation periodically interrupted by erosion.

The origin of carbon-rich sediments has different interpretations. Some researchers suppose that the burial of considerable OM mass in sediments was fostered by anoxic environments that prevented the destruction of OM in the basin (Demaison and Moore, 1980, 1991). Other researchers consider that the major role belongs to increase in bioproductivity of basins (Pedersen and Calvert, 1990, 1991). Based on scrutinization of this problem for the Holocene history of the Black Sea, Strakhov showed that the hydrosulfuric contamination is not crucial in the burial of large OM masses, though this factor may affect the qualitative OM composition. The increase in bioproductivity of basins is the main factor that is responsible for the substantial enrichment of sediments in OM (Strakhov, 1937, 1976, and others). The OM deposition at the beginning of the late Oxfordian could be fostered by the activation of phytoplankton bioproductivity probably due to increase in the concentration of biophile ele-

ments in the Oxfordian basin water. Paleogeographic features of Late Jurassic basins in the Russian Plate, as well as the local and short-term character of the Oxfordian episode, suggest that recycling and redistribution of biophile components within the basin was a result of fluctuations in the common system of basinal water circulation.

Results of the study of geochemistry of OM based on high-precision methods allow us to specify substantially the depositional environment of the Oxfordian carbon-rich rocks.

Organic Matter of Oxfordian Sediments

Bitumen fraction. The studied Oxfordian sedimentary rocks are distinguished by low chloroform-soluble bitumen (CB) concentrations ($\beta^{CB} = 0.6\text{--}1.4\%$ in the analyzed samples) as a result of low degree of catagenetic transformation of OM. The composition of *n*-alkanes and isoprenoids in the aliphatic fraction (F4) of bitumen is somewhat variable (Fig. 3) as follows from the results of gas chromatography. The bimodal distribution of *n*-alkanes is characterized by the prevalence of odd hydrocarbons in a wide molecular-mass range. Samples M-1/1 and M-1/4 with relatively low C_{org} concentrations contain bitumens enriched in *n*-alkanes of the $C_{15}\text{--}C_{17}$ composition, while the bitumen in OM-rich shales and clays is enriched in the higher-molecular *n*-alkanes ($C_{25}\text{--}C_{31}$). A similar pattern was detected in bitumens recovered from the middle Volgian rocks of the Sysol'sk shale-bearing district (Bushnev and Lyyurov, 2002). The prevalence of odd *n*-alkanes in the medium-molecular region is regarded as evidence for the contribution of marine phytoplankton to the initial OM (Tissot and Welte, 1978). The occurrence of high concentrations of odd *n*-alkanes in the high-molecular region is an indicator of the input of higher plant remains into the basin (Hunt, 1995).

The pristane/phytane (Pr/Ph) ratio as an indicator of redox conditions at the stage of early diagenesis (Peters and Moldowan, 1993) is low (0.1–0.6) in the studied samples and testifies to the reducing diagenetic setting. The total content of *n*-alkanes (mg/g C_{org}) varies in the studied section. Their concentration decreases two times while ascending from the calcareous clay to the carbon-rich shale and then increases upward the section. We can assume several mechanisms for the concentration of mainly low-molecular *n*-alkanes in the C_{org} -poor rocks, e. g., the migration of light HCs, different compositions of the initial OM, different chemical mechanisms of the conservation of *n*-alkyl chains in diagenesis, and the catalytic impact of clays, which is most effective at a low OM content in initial sediments.

The distribution of polycyclic biomarkers of the sterane and hopane series was studied with chromatographic mass spectrometry. Regular steranes in the aliphatic fraction of bitumen are largely represented by $5\alpha(H)$, $14\alpha(H)$, and $17\alpha(H)$ 20R modifications (Fig. 4). The

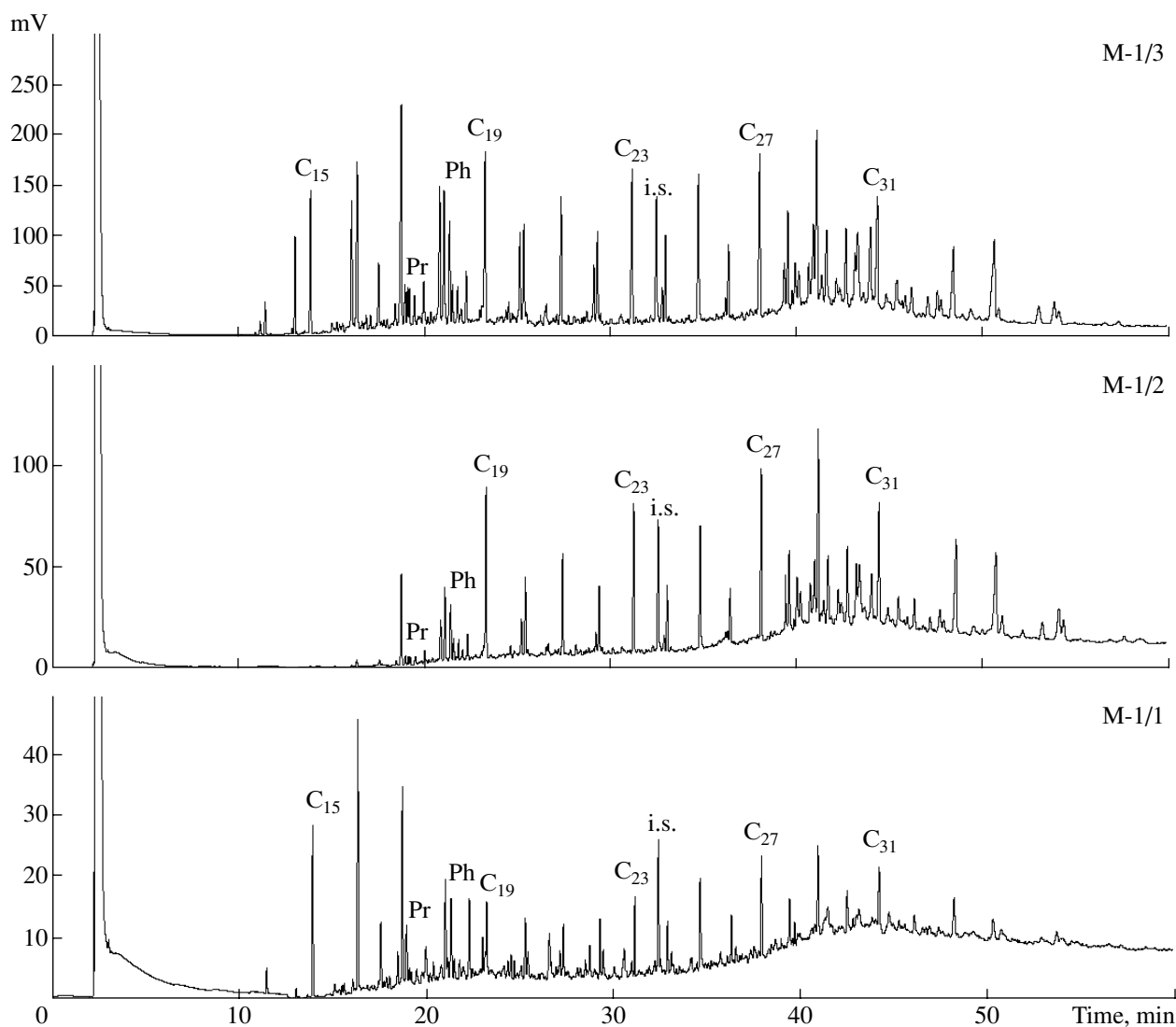


Fig. 3. Chromatograms of aliphatic fractions (F4) of bitumen from Oxfordian rocks. (C with subindex) *n*-alkane; (Pr) pristane; (Ph) phytane; (i.s.) internal standard..

high concentration of biological isomers of regular steranes indicates a low degree of catagenetic OM transformation. It is worthy to note that analysis of bitumen in the underlying oil shale has shown that steranes of the $\alpha\beta\beta$ configuration also occur therein. This phenomenon may be explained by the effective isomerization of steranes in the OM adsorbed on clay minerals. This is confirmed by the data on *n*-alkanes. The data on hopane hydrocarbons also indicate the low catagenetic maturity of OMs. Hopane hydrocarbons mainly occur in the bitumens as biological $17\beta(\text{H})$ and $21\beta(\text{H})$ 22R epimers. Concentrations of geohopanes ($\alpha\beta$) and moretanes ($\beta\alpha$) are considerably lower.

The distribution of steranes C_{27} – C_{29} (calculations are based on the $\alpha\alpha\alpha$ 20R epimer) is practically identical in all studied samples. The contents of steranes C_{27} and C_{29} are equal, while the share of sterane C_{28} is

much lower. The distribution of sterane HCs may be regarded as evidence for the commensurable contribution of marine phytoplankton and land plants to the initial OM composition (Waples and Machihara, 1991).

The chromatic mass spectrometry of aromatic fraction (F5) of bitumen did not reveal derivatives of isorenieratene, which is an aromatic carotenoid in the lipid fraction of green sulfuric photosynthesizing *Chlorobiaceae* bacteria. The detection of isorenieratene in bitumen indicates the hydrosulfuric contamination of photic layer of the paleobasin (Summons and Powell, 1987). The detection of derivatives of isorenieratene in the lower Aptian bituminous shale of the Middle Volga region (Bushnev, 2005) and in the middle Volgian oil shale of the *Dorsoplanites panderi* ammonite zone of the northern Russian Plate (Bushnev and Burdel'naya, 2003) indicate with a high degree of probability that water masses of these basins were contaminated with

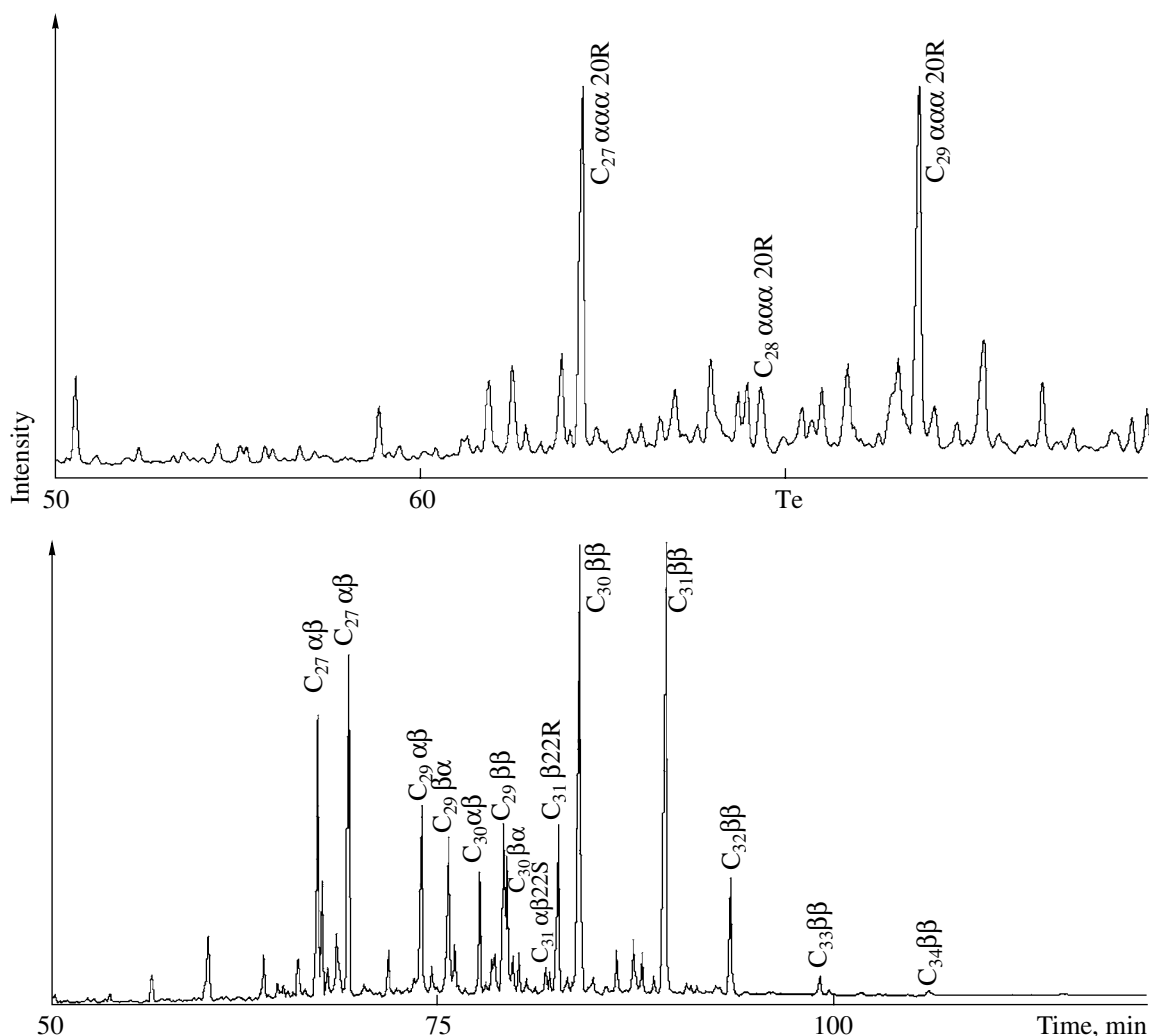


Fig. 4. Mass-chromatograms based on 217 sterane and 191 triterpane ions of the aliphatic fraction of bitumen from carbon-rich shales, sample M-1/2.

hydrogen sulfide. Let us note that the absence of isorenieratene derivatives may be related to not only normal aeration of the entire water column, but also subsidence of the O_2/H_2S boundary to a depth, which is inaccessible for the penetration of a sufficient amount of light for the photosynthesis of *Chlorobiaceae* (Repeta, 1993). Such an environment currently exists in the Cariaco Trough on the shelf of Venezuela (Aycard et al., 2003).

Kerogen: elemental composition. The atomic H/C ratio calculated from elemental analysis of kerogen varies from 0.51 to 1.08. Kerogen extracted from the clays that underlie oil shales contains a minimum amount of hydrogen, indicating the accumulation of OM in a well-aerated basin with the rewashing of sediments and their intense bioturbation. The abrupt change of H/C ratio in kerogen while passing to the overlying oil shale emphasizes the contrasting difference of OM burial environments in the initial sediments. The oil shale bed was deposited under reducing conditions. From the theoret-

ical point of view, such conditions could be related to increase in the mass of reactive OM in sediments or development of anoxic environment in the basin. Kerogen extracted from the overlying clay is characterized by medium H/C values, which point to deterioration of conditions for the OM retention in sediments.

Kerogen pyrolysates. The molecular composition of kerogen fragments can only be studied after its decomposition into the low-molecular compounds, for example, by pyrolysis or chemical destruction (Hold et al., 1998). Kerogen pyrolysates are usually represented by compounds of the following series: *n*-alkanes, *n*-alkenes-1, derivatives of benzene, thiophene, and others (Fig. 5).

The ratio of 2,3-dimethylthiophene to the sum of 1,2-dimethylbenzene and *n*-nonane-1, i.e., the thiophene ratio (TR), abruptly increases when passing from the lower clays to oil shales and then gradually decreases upward the section (table). The measurement

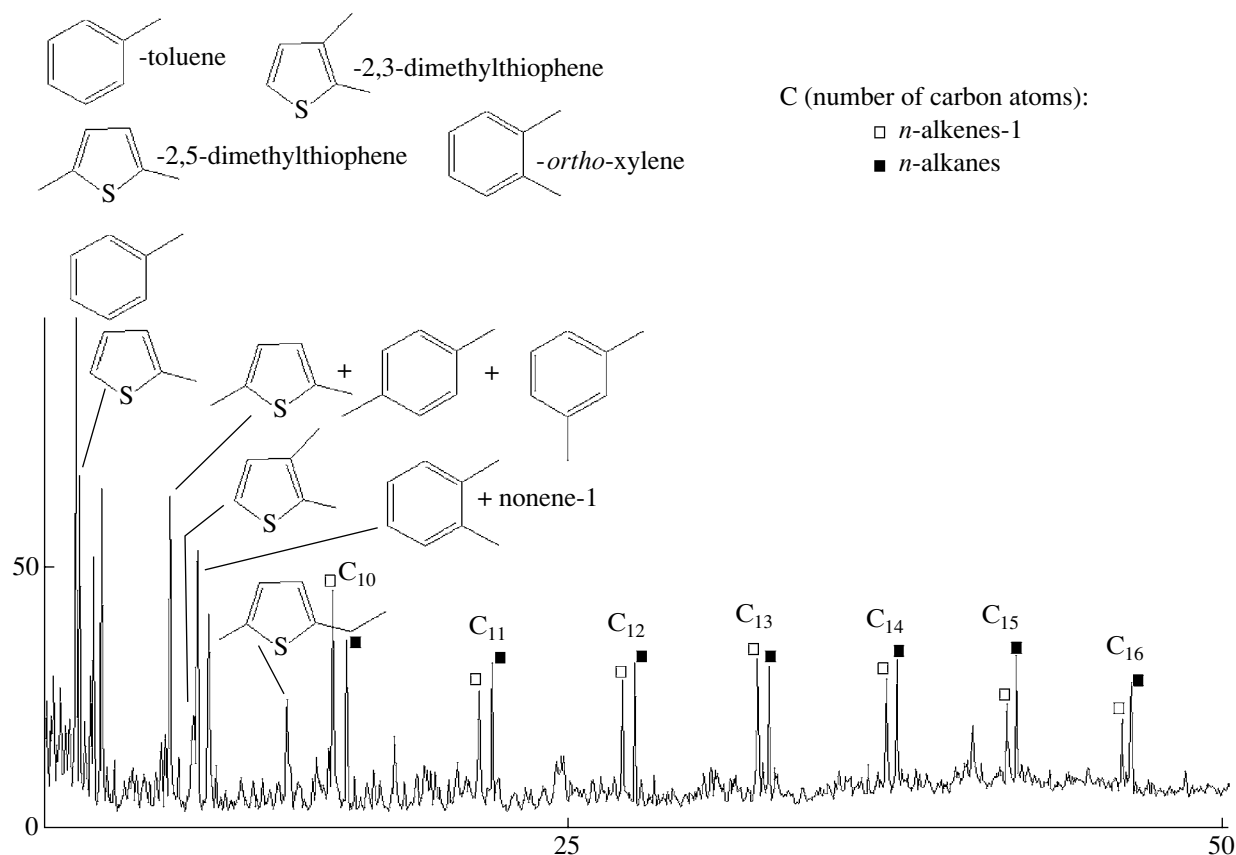


Fig. 5. A segment of mass-chromatogram of kerogen pyrolysates of carbon-rich shales (sample M-1/2) based on the total ionic current and selected structures of aromatic and sulfuric compounds identified in kerogen pyrolysates.

of TR values in kerogen pyrolysates is an express technique used to determine the atomic S_{org}/C ratio of kerogen (Eglinton et al., 1990). The higher S_{org}/C ratio in kerogen from shales, relative to its counterpart in the underlying clays, testifies to a more intense sulfurization of OM during the early diagenesis of carbon-rich sediments. Decrease of the S_{org} content in kerogen from the overlying clay indicates the attenuation of sulfurization in the OM-depleted clay.

The 2,5-DMT/(2-ET + 2,4-DMT + 2,3DMT) ratio (DMT is dimethylthiophene and ET is ethylthiophene), which is calculated from the composition of C_2 -replaced thiophenes and correlated with contents of polysulfidized sugar residues in the kerogen structure (Van Kaam-Peters et al., 1998), does not reveal a significant correlation with the C_{org} content in rock, the atomic H/C ratio in kerogen, or the thiophene ratio. It may be suggested that the formation of kerogen in the Oxfordian rocks is not related to the conservation of hydrocarbon components of the initial OM owing to its sulfurization. Conversely, the study of middle Volgian and Lower Cretaceous sedimentary rocks of the Russian Plate showed that this process markedly affected the formation of kerogen (Bushnev and Burdel'naya, 2003; Bushnev, 2005).

The phenols/thiophenes ratio calculated according to the technique reported in (Bushnev, 2001) reveals a strong negative correlation with the atomic H/C ratio of kerogen ($R = -0.95$). Phenols in the pyrolysate are considered products of the thermal destruction of lignin and its constituents. Thus, relative increase in the concentration of phenols together with decrease in the H/C ratio of kerogen indicates relative increase in the contribution of higher plants into the OM of C_{org} -depleted clays.

n-alkanes and *n*-alkenes-1 are the main components of aliphatic fraction (F3) of kerogen pyrolysates (Fig. 6). The distribution and concentrations of *n*-alkanes and *n*-alkenes-1 in kerogen pyrolysates vary across the section. The sum of *n*-alkanes and *n*-alkenes-1 is clearly correlated with the atomic H/C ratio ($R = 0.80$) and thiophene ratio of kerogen pyrolysates (TR is proportional to S_{org}/C , $R = 0.98$). Thus, kerogen in the Oxfordian C-, H-, and S-rich shale was largely formed due to the sulfurization and conservation of the lipid fraction of the initial OM. Figure 6 shows that the distribution of *n*-alkanes and *n*-alkenes-1 in pyrolysates of the C_{org} -depleted clayey rocks (samples M-1/1 and M-1/4) appreciably differs from the distribution in oil shales and C_{org} -rich clays (samples M-1/2 and M-1/3).

Composition of organic matter in the Oxfordian rocks

Index	Sample			
	M-1/1, gray clay	M-1/2, carbonaceous shale	M-1/3, OM-rich clay	M-1/4, gray clay
Bituminological characteristic				
C _{org}	0.90	12.99	5.63	0.94
CBA, %	0.007	0.177	0.067	0.006
β ^{CB} , %	0.8	1.4	1.2	0.6
Composition of bitumen				
Pr/Ph	0.57	0.08	0.33	n.d.
Oddness index (I)*	1.04	2.49	1.62	1.13
Oddness index (II)**	2.10	2.49	2.61	2.52
Σ _n -alkanes, mg/g C _{org}	0.14	0.07	0.11	0.16
Σ _{isoprenoids} , mg/g C _{org}	0.02	0.003	4250.011	n.d.
Composition of kerogen and its pyrolysates				
H/C	0.51	1.09	0.79	0.80
TR***	0.05	0.31	0.21	0.09
S _{org} /C****	0.003	0.021	0.014	0.006
2,5DMT/(2ET + 2,4DMT + 2,3DMT)	0.60	0.80	0.63	0.77
Phenols/thiophenes	0.73	0.30	0.41	0.43
Σ _n -alkanes + <i>n</i> -alkenes-1, mg/g C _{ker}	1.02	2.94	2.17	0.90
Σ _{2-methyl-5-n-alkylthiophenes} , mg/g C _{ker}	n.d.	0.066	0.046	0.008
H ₂ , mg/g C _{ker}	2.22	1.80	1.90	2.56
CO, mg/g C _{ker}	42.90	30.96	39.63	63.55
CH ₄ , mg/g C _{ker}	7.46	24.75	22.89	8.97
CO ₂ , mg/g C _{ker}	163.49	66.03	94.09	267.36
C ₂ H ₄ , mg/g C _{ker}	0.91	6.50	6.15	5.25
C ₂ H ₆ , mg/g C _{ker}	1.53	10.49	9.40	2.91

* Oddness index (I) = $2n-C_{17}/(n-C_{16} + n-C_{18})$.

** Oddness index (II) = $2n-C_{29}/(n-C_{28} + n-C_{30})$.

*** TR = 2,3-dimethylthiophene/(1,2-dimethylbenzene + *n*-nonene-1).

**** Estimated from TR value with allowance for the curve in (Eglington et al., 1990); (n.d.) no data.

The C_{org}-depleted rocks are characterized by the prevalence of even structures C₁₄, C₁₆, C₁₈, and C₂₀. The even *n*-alkyl structures also predominate (but to a much lesser extent) in oil shales and C_{org}-rich clays. The *n*-alkyl chains of kerogens in C_{org}-rich rocks (samples M-1/2 and M-1/3) are probably derived from fragments of algaenan, which is a biochemical component of marine algae that consists of long *n*-alkyl chains connected by simple and complex ether bonds (Gelin et al., 1996, 1999). According to (Blokker et al., 1998), precisely algaenan provides the uniform distribution of *n*-alkane and *n*-alkene-1 pairs in the course of pyrolysis. The *n*-alkyl chains of kerogens in the C_{org}-depleted clay (samples M-1/1 and M-1/4) are mainly represented by low-molecular fragments that entered the kerogen composition in the process of condensation of even fatty acids and alcohols.

The aromatic fraction (F4) of kerogen pyrolysates contains a wide range of hydrocarbon and heteroatomic

compounds. Sulfuric components of the aromatic fraction are represented by 2-*n*-alkylthiophenes, 2-methyl-5-*n*-alkylthiophenes, and benzthiophenes with various alkyl substitutions. Concentration of 2-methyl-5-*n*-alkylthiophenes in the M-1/2 shale pyrolysates is 0.066 mg/g C_{ker} (table). Concentration of the same components is 0.19 mg/g C_{ker} in pyrolysates of the Aptian bituminous shale from the Russian Plate (Bushnev, 2005) and 0.15–0.50 mg/g C_{ker} in the Volgian oil shale from the Sysol'sk district (Bushnev and Burdel'naya, 2003). Hence, the content of sulfur-bound *n*-alkyl fragments of kerogen (precursors of *n*-alkylthiophenes of the pyrolysate) in the Oxfordian oil shale is hundreds of times lower than that in the coeval carbon-rich shale of the Russian Plate formed in paleobasins with hydrosulfuric contamination of water. Processes of sulfate reduction in the Oxfordian carbon-rich sediments were apparently less intense. Therefore, they did not lead to

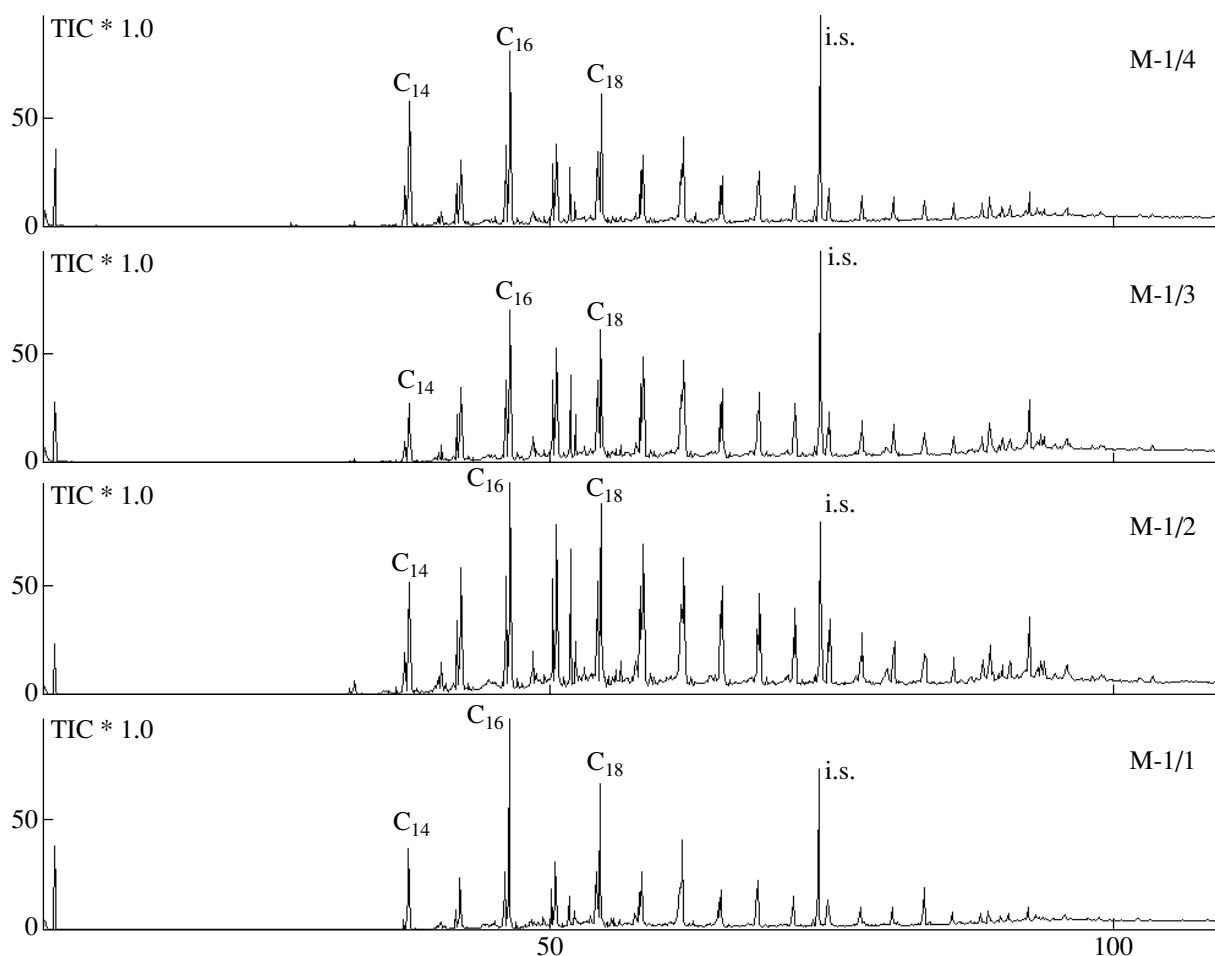


Fig. 6. Mass-chromatograms based on the total ionic current of aliphatic (F3) fractions of kerogen pyrolysates. (C with subindex) Pairs of *n*-alkene-1 and *n*-alkane peaks; (i.s.) internal standard.

intense sulfurization of OM and steady hydrosulfuric contamination of water in the paleobasin.

Gases in kerogen pyrolysates. Gas components of kerogen pyrolysates are represented by H_2 , CO, CO_2 , H_2S , H_2O , CH_4 , C_2H_4 , C_2H_6 , and heavier hydrocarbons (table). The table shows that variations in the gas composition across the section are related to variations in the elemental composition of kerogen and C_{org} content in rocks. The highest contents of oxygen-bearing gases (CO and CO_2), which are products of the thermal breakdown of mono- and dioxygen-bearing functional groups (Bushnev and Shanina, 2005), are recorded in the H-poor kerogen pyrolysates extracted from the C_{org} -depleted clayey rocks with the most oxidized OM. In contrast, the output of gaseous hydrocarbons is maximum in the H-rich kerogen pyrolysates extracted from oil shales and the overlying C_{org} -rich clay.

It is worthy to compare the compositions of gases released in the course of pyrolysis from the under- and overlying clays (samples M-1/1 and M-1/4, respectively). The C_{org} content is similar in these samples, but kerogen from the overlying clay is markedly enriched

in hydrogen. Let us note that kerogen from the underlying clay (sample M-1/1) releases much less oxygen-bearing gases than kerogen from the overlying clay (sample M-1/4). This is inconsistent with the relative H-enrichment of the latter kerogen. We assume that this circumstance reflects different types of the origin of kerogen in clays. The overlying clay probably contains the thermally (catagenetically) immature marine kerogen that is syngenetic to the host clay but substantially oxidized. Therefore, it is characterized by higher contents of both hydrogen and oxygen-bearing structural groups. In the underlying clay, OM is largely represented by components redeposited from older rocks. These intensely transformed components lost hydrogen and oxygen at the preceding stage of burial. The similar distribution of biomarker-hydrocarbons in clay samples M-1/1 and M-1/4 may be related to mixing of the marine syngenetic OM, which is responsible for the hydrocarbon composition of bitumen in the underlying clay (M-1/1), and the redeposited inert OM, which is responsible for the bulk attributes of kerogen and its pyrolysates.

CONCLUSIONS

(1) The upper Oxfordian carbon-rich sedimentary rocks of the Russian Plate are close to the middle Volgian oil shale *Dorsoplanites panderi* in terms of the C_{org} content and lithology, but they are distinguished by a narrow stratigraphic and regional distribution.

(2) The low degree of catagenetic maturity of OM in the Oxfordian rocks is confirmed by the following features: (i) the composition of diastereomers of sterane and hopane hydrocarbons is largely represented by biological forms ($\beta\beta$ in hopenes and $\alpha\alpha\alpha$ in steranes); (ii) coefficient β^{CB} is low, while the concentration of odd n -alkanes is high within a wide molecular-mass range. Thus, the geochemical signatures of OM in the Oxfordian rocks are related to synsedimentary and early diagenetic processes.

(3) The initial OM in the Oxfordian clay, which hosts the carbon-rich rocks, was represented by a mixture of marine phytoplankton and land plant remains. However, the marine OM was not apparently retained. The proportion of phytoplankton remains significantly increased in the C_{org} -rich shale and clay.

(4) The C_{org} -rich unit was formed as a result of the short-term abrupt rise of phytoplankton bioproductivity during an episode of relative eutrophication of water in the Oxfordian paleobasin, probably, owing to the recycling and redistribution of biophile elements.

(5) The marine OM in carbon-rich sediments was transformed mainly under reducing conditions characterized by biochemical sulfate reduction. This is evident from the appreciable sulfur concentrations when passing from host clays to the carbon-rich rocks. The main mechanisms of the bonding of reduced sulfur in sediments were realized in the course of its incorporation into organic compounds of the lipid fraction of the initial OM (sulfurization). This is indicated by the occurrence of sulfurorganic compounds in kerogen pyrolysates.

(6) Paleoecological conditions near the marine water/sediment interface were variable during the deposition of carbon-rich sediments. At the initial stage of their deposition, the conditions were unfavorable for the permanent habitat of burrowing organisms. This is evident from the scarcity of bioturbation tracks in the carbon-rich shale. The situation was normalized during the subsequent deposition of the C_{org} -rich clay. However, no stable anoxic environment (hydrosulfuric contamination) existed in the watermass, as suggested by the absence of isorenieratene derivatives in the bitumen fraction of OM from carbon-rich rocks. This conclusion is consistent with the relatively low (in comparison with the nearly coeval carbon-rich shales of the Russian Plate) concentration of redox-sensitive chemical elements (S, Mo, and V) in the Oxfordian carbon-rich rocks. Probably, adsorption on particles of suspended OM was the main mechanism of concentration of these elements in the carbon-rich sediments.

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