Biogeochemistry and microfossils of the Upper Jurassic and Lower Cretaceous, Anabar Bay, Laptev Sea

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Abstract

A detailed analysis of organic matter from the Oxfordian–Lower Valanginian interval of the Nordvik section (Anabar Bay) allows the definition of three geochemical horizons (terpane, diasterene, and hopane), which are characterized by specific geochemical compounds and their ratios. These horizons are correlated with several stages in the evolution of microfossils associated with ecological and geochemical changes in sea paleobasin. Our study shows a good correlation among the variation in many geochemical parameters, the composition of microfossil assemblages, and the transgressive-regressive phases of the paleobasin evolution. Moderately shallow-water facies was reconstructed using micropaleontological, palynological, and lithological data from the upper and lower parts of the section, where the terpane and hopane horizons were identified. Both horizons are characterized by a general dominance of hopanes over other polycyclic biomarkers, the presence of compounds with the biological configuration and organic matter of mixed terrestrial-marine origin, the presence of benzohopanes and retene, an indicator of the conifer resins. This is also reflected in the composition of palynological assemblages, which are dominated by terrestrial palynomorphs, with rare conifer pollen grains. Relatively deep-water facies were identified in the middle part of the section (diasterene horizon). A distinctive geochemical feature of this interval is high relative abundances of diasterenes and 4-methyldiasterenes. The lower subhorizon is characterized by the highest values of the pristane/n-C_{17} ratio and relatively light $\delta^{13}C$ values of noncarbonate carbon. The aromatic fractions have anomalously high concentrations of methyltrimethyltridecylchromans (MTTCs), which are interpreted to be derived mostly from chlorophyll of prasinophytes. The terpenoid distribution is marked by the presence of neohop-13(18)-enes, which probably originated from the activity of methanotrophic bacteria. The above geochemical parameters indicate high photic zone productivity (which is confirmed by the composition of palynological assemblages with abundant dinocysts and prasinophytes) that favored the accumulation of organic matter in dysaerobic conditions, which periodically occurred in the bottom of paleobasin. The alternation of dysaerobic and low-oxic bottom water conditions is easily reconstructed from the analysis of microbenthic communities. The analysis of biogeochemical, micropaleontological, paleontological, and palynological data on the Upper Volgian–lowermost Berriasian organic-rich shales revealed a very good source rock potential for this part of the section, as indicated by relatively high concentrations of organic matter of mixed bacterial-algal genesis and stagnant conditions during deposition and diagenesis. However, this potential was not realized because of the extremely "mild" thermobaric conditions that existed within the Mesozoic strata of the present-day Anabar Bay. At the same time, our results and analysis of the available data allow an optimistic assessment of the hydrocarbon potential of Jurassic–Lower Cretaceous deposits on the Laptev Sea shelf.
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Introduction

The Late Jurassic–Early Cretaceous was marked by large-scale global deposition of organic carbon-rich sediments that play an important role as source rock formations in sedimentary basins of various sizes and origin (Kontorovich, 2004; Neruchev, 1974). In the Jurassic–Cretaceous section of the Anabar Bay (Fig. 1), the organic-rich shales of the Urdyuk-Khaya and Paksa Formations were also formed due to this global event.

In the north of the Siberian Platform, widespread Upper Jurassic and Cretaceous shales and siltstones have been well studied within marginal depressions (Verkhoyansk, Lena–Anabar, and Yenisei–Khatanga troughs, Anabar–Khatanga saddle) in in several outcropes and recovered by extensive drilling. It allowed to study the main types of sedimentary

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sections, which became the basis for the development of zonal stratigraphic scales using different groups of macro- and microfossils, marine and terrestrial palynomorphs (Nikitenko et al., 2011, 2013, 2015a,b; Peshchevitskaya, 2010; Shurygin and Dzyuba, 2015).

A wealth of organic geochemical data are available from studies of selected intervals of the Mesozoic sections, which allow a correlation with different microfossils (microphytoplankton, terrestrial palynomorphs, foraminifers, and ostracods) and are also important for determining the type of dispersed organic matter (OM), its depositional conditions, diagenetic and catagenetic evolution, and thermal modification into hydrocarbons (HC) of the petroleum series.

In this paper, we present the results of an integrated geochemical, micropaleontological and palynological investigation of the reference section for the Upper Jurassic and Lower Cretaceous at Cape Urdyuk-Khaya, Nordvik Peninsula (Fig. 1). Here, an interrupted and continuous section spanning the Upper Oxfordian–Lower Valanginian with abundant macro- and microfossils is well exposed along the coastal cliffs. The analysis of the stratigraphic distribution of ammonites, foraminifers, ostracods, marine microphytoplankton and terrestrial palynomorphs from this section (Nikitenko, 2009; Nikitenko et al., 2008, 2011, 2013, 2015a,b; Peshchevitskaya, 2010) allowed us to establish and refine zonal scales for the Upper Jurassic and Lower Cretaceous based on microfossils and to provide models for the basin evolution. The section is composed of dark gray, often glauconitic shales of the Urdyuk-Khaya Formation (Upper Oxfordian–Middle Volgian), brownish to dark gray shales of the Paksa Formation (Upper Volgian–Valanginian) and is well exposed in the axial part and flanks of the Urdyuk-Khaya brachyanticline (Fig. 1). Both micropaleontological and palynological characteristics of this section are discussed in details in a number of previous papers (Nikitenko, 2009; Nikitenko et al., 2008, 2013, 2015a,b; Peshchevitskaya, 2010), which provide an overview of the sample preparation techniques for micropaleontological and palynological analyses and the basic methodology used in paleofacies reconstruction.

This study provides an integration of data from micropaleontological and palynological assemblages, which help in the reconstruction of transgressive–regressive events as well as many different parameters of a paleobasin, such as temperature, salinity, dissolved oxygen, paleoenvironments, and climatic conditions (Fig. 2) for different time intervals. This allowed us to reconstruct the evolution of these parameters and correlate them with variations in specific geochemical parameters. The geochemical stratification indicated by organic geochemical criteria was taken as a basis and extended to reflect the trends in the distribution of microfossils and palynomorphs, as well as the evolution of paleofacies in the basin's history.

Geochemical methods

Samples of argillaceous rocks utilized for organic geochemistry were first crushed using a ball mill and then separated into several portions. The main portion was used for chloroform extraction, while the remaining samples were treated with hydrochloric acid and subsequent determination of the insoluble residue (IR), total organic carbon (C_{org}), stable carbon isotopic composition ($\delta^{13}C$) and the evaluation of the pyrolysis data. The concentration of total organic carbon was determined using an AN-7529 analyzer. Pyrolysis data were obtained using an SR Analyzer—POPI. The $\delta^{13}C$ values of the carbonate-free residues were measured on an MI1201V mass spectrometer.

Asphaltenes were removed from the dichlormethane extract by precipitation using excess petroleum ether and then fractioned into resins, aliphatic and aromatic hydrocarbons by liquid chromatography using alumina/silica gel columns.

The hydrocarbon fractions were analyzed by gas chromatography–mass spectrometry using the Agilent GC/MS system consisted of a HP6890 gas chromatograph interfaced with an Agilent 5973N mass selective detector. The chromatograph was equipped with the HP-5MS capillary column (length 30 m and inner diameter 0.25 mm) and operated in constant flow mode (at 1 mL/min) with helium as carrier gas. The injector temperature was 300 ℃, and samples were injected in splitless mode. The temperature program was 100–290 ℃ at 4 ℃/min, held at 290 ℃ for 20 min. The instrument was operated with an electron energy of 70 eV and a temperature of 230 ℃. In addition to TIC chromatograms the SIM signals were also monitored by selecting fragment ions (*m/z* is the ratio of the ion's mass to its charge). Identification of the individual compounds was done on the basis of NIST-08 library search (over 130 thousands mass spectra of organic compounds), by comparing with literature data and reconstruction of structures based on the nature of ion fragmentation during electron impact (Kashirtsev et al., 2012).

The relative concentrations of the individual constituents were calculated by integrating their peak areas on individual and composite chromatograms using the autointegrate capability of the MSD-DATA Data Analysis program.

Geochemical and biofacies characterization of the section

The key geochemical parameters (Table 1) used in this study include the organic carbon content (C_{org}), pyrolysis characteristics of organic matter (Tmax, S1, S2, HI), carbon isotope composition ($\delta^{13}C$) of a residue insoluble in hydrochloric acid (IR), the composition and distribution of normal alkanes, isoprenoids, terpanes and steroid hydrocarbons, as well as some secondary biomarkers in the aromatic fractions. Notable variations in the distribution of biomarker molecules from old to young strata can be clearly seen on the *m/z* 191, 217, 257, 271 composite mass chromatograms of the aliphatic fractions (terpanes, steranes, diasterenes, and 4-methyldiaster-