Diatom biomarkers during the Eocene/Oligocene transition in the Il'pinskii Peninsula, Kamchatka, Russia

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Abstract

Marine strata of the Il’pinskii section, northeastern Kamchatka, Russia, expose the complete Eocene/Oligocene (E/O) succession. Although diatom fossils are very poorly preserved in these mudstones and carbonate concretions, Oligocene mudstones contain typical diatom biomarkers, the C_{25} highly branched isoprenoids (HBIs), in concentrations that rise markedly above the E/O boundary. The abundance of the dinoflagellate biomarkers known as dinosteranes decreases through the late Eocene to Oligocene interval. A rise in the abundance of HBIs through this time interval suggests that the post-E/O diatom community of the northwest Pacific region was dominated by the genus *Rhizosolenia*. HBIs in sedimentary rocks spanning the E/O transition may show the appearance of the Oligocene marine diatom *Rhizosolenia oligocaenica*, and may therefore be useful as biomarkers in regional biostratigraphic correlation of the

northwest Pacific during this interval. An E/O boundary in the Il’pinskii section is proposed based on HBI distribution.

Keywords: Paleogene; highly branched isoprenoid; HBI; diatom biomarker; Eocene/Oligocene boundary; Kamchatka

1. Introduction

The Cenozoic is a time of global cooling. The Eocene–Oligocene (E/O) interval was a critical time in Earth's climatic history during which a transition from greenhouse to icehouse conditions took place. During the 10-my interval from the middle Eocene to the early Oligocene, deep ocean and surface waters at high latitudes cooled (e.g., Zachos et al., 2001). This rapid cooling is reflected in a faunal turnover in marine and terrestrial biotas (e.g., Prothero and Berggren, 1992). At a global scale, a positive shift in benthic foraminiferal $\delta^{18}O$ values just above this boundary, called the Oi1 event (Miller et al., 1991), occurred at the same time as the opening of the Tasmanian gateway, which resulted in an increase in surface-water productivity and a change from calcareous-microfossil-rich sediment to biosiliceous ooze (Kennett et al., 1975; Kennett, 1977; Diester-Haass, 1992, 1995, 1996; Diester-Haass and Zahn, 1996; Salamy and Zachos, 1999). Throughout the Cenozoic, diatoms tolerant of such chaotic conditions increased in diversity relative to other phytoplankton (e.g. Falkowski et al., 2004).

Information about E/O boundary biotic events in the high-latitude North Pacific is lacking, however, due to a dearth of continuous stratigraphic sections that contain abundant diatom fossils (Baldauf and Barron, 1990).

Diatom fossils were obtained from late Oligocene sedimentary rocks in the Navarin Basin Province, Bering Sea, by Baldauf and Barron (1987), and detailed studies of Oligocene diatoms from Komandorski Island in the high-latitude North Pacific were undertaken by Gladenkov (1998, 1999). Gladenkov and Gladenkov (2007) recently found biostratigraphically useful diatom remains in casts of fossil mollusks and in carbonate concretions from the Paleogene marine succession of the Il'pinskii Peninsula. In spite of these advances, a complete E/O succession with a robust diatom record has not yet been documented from the North Pacific region.

Poor preservation of siliceous diatom frustules commonly precludes unambiguous taxonomic identification. More than 90% of suspended biogenic silica is dissolved and recycled in the water column, and does not become part of the sedimentary record. Diatom frustules are easily destroyed by the transformation from opal-A to opal-CT during diagenesis (Hein et al., 1978). The generally poor diatom record for the E/O transition interval may be predominantly due to the unstable nature of diatom frustules. As a result, abundance and diversity patterns for North Pacific diatom communities during the E/O transition remain poorly understood.

Biomarkers of zoo- and phytoplankton, eubacteria, and archaea in sedimentary rocks have been applied to reconstructing paleoenvironments and paleoecological systems. Among the various biomarkers, the highly branched isoprenoid (HBI) alkenes are known to be produced by a limited range of diatom species. The genus *Rhizosolenia*, for example, can produce either C_{25} and/or C_{30} HBI alkenes (Volkman et al., 1994; Sinninghe Damste et al., 2004). Diatom biomarkers in sedimentary rocks may provide clues to the variations in diatom community and biomass during the E/O transition in the North Pacific.

This paper focuses on HBIs in sedimentary rocks spanning the E/O transition. A succession of marine sedimentary rocks exposed at the Il’pinskii section, Kamchatka Peninsula, Russia, includes the E/O boundary, as indicated by assemblages of benthic mollusks and foraminiferans (Beniamovskii and Gladenkov, 1996; Gladenkov and Gladenkov, 2007) as well as magnetic polarity (Minyuk and Gladenkov, 2007). The latter data indicate that the long reverse-polarity interval Chron 12r is very compressed in this area. The Eocene Kilakirnun and Gailkhavilanvaym Formations consist of marine turbiditic sandstone and mudstone. The Early Oligocene Alugivayam Formation consists predominantly of hemipelagic siltstones. The E/O boundary has been defined by the disappearance of the foraminiferan *Caucasina eocenica* Kamchatika Zone (Serova, 1976) and by mollusk biostratigraphy (Kafanov and Ogasawara, 2004). The general geology and benthic faunas of the Kamchatka region have been described by Gladenkov (1980). Stratigraphic variation in diatom production as revealed by biomarker analysis for sedimentary rocks from the Il’pinskii section would help to elucidate diatom evolution during the E/O transition, as well as possibly provide globally relevant biostratigraphic information.

2. Materials and methods

2.1. Geological setting and samples

Paleogene marine sedimentary rocks, including the E/O transition (Serova, 1976; Kovalenko, 1992; Gladenkov and Shantser, 1993; Maxwell and Chinakayev, 1999) are well exposed in the Il'pinskii section of the Kamchatka central basin, on the eastern side of the Kamchatka Peninsula, Russia (Fig. 1). The Paleogene succession is about 2500 m thick and is divided into the Yuzhnoilpin, Kylan, Kilakirnun, Gailkhavilanvaym, and Alugivayam Formations. Thirty-seven mudstone samples from the Kilakirnun and Gailkhavilanvaym Formations (Eocene) and the Alugivayam Formation (Oligocene) at the Il'pinskii section were used for the present study.

2.2. Experimental procedures

Samples were crushed and pulverized to finer than 200 mesh size in preparation for geochemical analysis. Total organic carbon (TOC), inorganic C (IC), total nitrogen (TN), and total sulfur (TS) were determined using the EA3000 CHN analyzer (EuroVector Co., Milan, Italy). The samples were weighed and placed in a silver capsule with a few drops of 1 N HCl to remove any carbonate. The sample was then dried at 120°C for 2 h and placed into a tin capsule. All elemental compositions reported are on a dry weight basis. The error of C, N, and S analysis was ±3% for TOC and TN, and ±5% for TS, respectively.

X-ray fluorescence (XRF) spectrometry was performed to determine the inorganic elemental composition. Major elements, SiO_2, Al_2O_3, and Fe_2O_3 were analyzed using an energy-dispersive X-ray fluorescence spectrometer (JSX3211; JEOL, Tokyo, Japan) and pressed powder tablets of 20 mm i.d. The rhodium tube was set at 30 kV and 0.2 mA.

Elemental composition was quantified with reference to the standard samples, JA-1, JA-2, JA-3, JCh-1, JG-2, JGb-1, JR-1, JR-3 and JSl-1 (Imai et al., 1995, 1996, 1999). Repeated XRF analysis gave standard deviations of 0.9% for SiO_2, 0.4% for Al_2O_3, and 0.2% for Fe_2O_3.

The lipid fraction was obtained by solvent extraction (15 min) with dichloromethane/methanol (1:3), dichloromethane/methanol (1:1), and dichloromethane using a BIORUPTOR RD-1 ultrasonic cell crusher (Cosmo Bio Co., Tokyo, Japan). The aliphatic hydrocarbon fraction was eluted with hexane using silica-gel column chromatography (gel Q-23; Wako, Osaka, Japan). The hydrocarbon fraction was analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). GC was performed using an HP6890 GC (Hewlett–Packard, Palo Alto, CA, USA) equipped with a splitless injector, fused silica capillary column (HP-5, 30 mm × 0.25 mm; J&W Scientific Inc., Folsom, CA, USA) and flame ionization detector. Helium was the carrier gas. The oven temperature for the GC was programmed for 2 min at 50ºC, then increasing from 50ºC to 300ºC at 4ºC/min, and finally 20 min at 300ºC. GC–MS was carried out using HP6890 GC with a fused silica capillary column (HP-5, 30m × 0.25 mm; J&W Scientific Inc.) and HP5973 inert XL mass selective detector (MSD) operated at 70 eV with a mass range from m/z 50 to 550. The same oven temperature program was applied to GC–MS analysis.

3. Results and discussion

3.1. Sedimentary facies and geochemical characteristics

Eocene to Oligocene marine sedimentary rocks exposed in the Il'pinskii section consist predominantly of silty mudstone with carbonate concretions (Fig. 2). Eocene mudstone samples are from the upper part of the Eocene Kilakirnun Formation (2 samples), and the Gailkhavilanvaym Formation, which conformably overlies the Kilakirnun Formation. The lower part of the Gailkhavilanvaym Formation is characterized by glauconitic sandstone and by the Laperalamskii tuff at its base (Fig. 2). The Oligocene mudstone samples are from the

Alugivayam Formation, which conformably overlies the Gailkhavilanvaym Formation. Volobueva et al. (1994) and Gladenkov and Gladenkov (2007) place the contact of the Gailkhavilanvaym and Alugivayam Formations 120 m below the base of the Mulatkhanskii Sandstones, which are intercalated with the lower part of the Alugivayam Formation. According to the same authors, the E/O boundary is tentatively located at the boundary of Gailkhavilanvaym and Alugivayam Formations, where changes in benthic faunal assemblages are noted. In the present paper, the contact of the Gailkhavilanvaym and Alugivayam Formations and the E/O boundary are placed close to the base of the Mulatkhanskii Sandstones (Fig. 2), for reasons to be discussed below.

XRF analyses of mudstone samples from the Il'pinskii section showed that SiO_2 concentration generally ranges from 62.5 to 71.4%. Other major inorganic elements are Al_2O_3 and Fe_2O_3, which range from 11.8 to 16.4% and 5.5 to 9.7%, respectively. The SiO_2 concentration is high compared to that of average shale (58.9%; Wedepohl, 1971), whereas

Al_2O_3 and Fe_2O_3 concentrations are generally lower than those of average shale. Some mudstones are rich in CaO and inorganic C, indicating the presence of carbonate minerals. Such calcareous mudstones are most common in the Kilakirnun and Gailkhavilanvaym Formations. Stratigraphic variations of SiO_2, Al_2O_3, and Fe_2O_3 contents are not pronounced (Table 1).

The TOC, TN, TS, and IC of the samples are shown in Table 1. The carbon to nitrogen (C/N) ratio, and carbon to sulfur (C/S) ratio of the samples are shown in Fig. 3. The TOC concentration ranges from 0.3 to 0.9%, and has no significant stratigraphic variation. Mudstone samples from the Eocene Gailkhavilanvaym Formation are characterized by high C/N ratios (10 to 20), whereas those from the Eocene Kilakirnun Formation and the Oligocene Alugivayam Formation have comparatively low C/N ratios of less than 10. Marine organic matter is generally characterized by C/N ratios in the range of 6 to 9, whereas the C/N ratio of terrestrial higher plant is much higher (Krishnamurthy et al., 1986; Meyers and Ishiwatari, 1993). Comparatively higher C/N ratios of mudstones from the Eocene Gailkhavilanvaym Formation, therefore, indicate a significant contribution from terrestrial organic matter, which could be related to a contribution from turbiditic sandstones and mudstones. The C/N ratios of Kilakirnun and Alugivayam Formation mudstones are low (generally <10), suggesting a greater contribution from marine planktonic organic matter.

C/S ratios of mudstones from the Il’pinskii section range from 1.0 to 3.5, with the exception of those around the contact of the Gailkhavilanvaym and Alugivayam Formations. These values are close to the average C/S ratio of normal marine mudstones (Raiswell and Berner, 1986). The C/S ratio is related to both oxic/anoxic conditions and salinity in the water column (Berner and Raiswell, 1984; Muller, 2001). The high C/S ratio in the vicinity of the contact of the Gailkhavilanvaym and Alugivayam Formations suggests the abrupt formation of suboxic to oxic depositional conditions during the E/O transition.

3.2. Organic maturity

The sedimentary rocks from the Il'pinskii E/O transitional section are poor in microfossils, likely due to their dissolution during settling and early diagenesis. Organic sediment constituents may be a useful substitute for microfossils in reconstructing the paleo-oceanic conditions at the time of sediment deposition. To this end, molecular parameters and source-specific biomarkers from mudstones were used. Thermal maturity of the samples was first evaluated because biomarker distribution is generally sensitive to thermal maturation. In the material analyzed, the C_{24} to C_{34} *n*-alkanes show odd carbon-number predominance (Table 2). The carbon preference index (CPI) of *n*-alkanes (C_{24} to C_{34}) is commonly used to estimate the maturity of sedimentary organic matter, although it can also be a function of organism type. The CPI results show no systematic stratigraphic variation and are in the range of 1.2 to 2.6 (generally >1.5), indicating that the samples are thermally immature. The sterane isomer ratio, 20S/(20S + 20R)-C_{29}, is also well known as a maturity parameter (Mackenzie and McKenzie, 1983; Suzuki, 1984, 1990). In the material analyzed, sterane isomer ratios are generally less than 0.1, indicating low thermal maturity (Table 2). Both CPI values and biomarker isomer ratios indicate a comparatively low degree of organic maturation (not near the oil window), and so thermal maturity is not a consideration in the discussions to follow.

3.3. Highly branched isoprenoids in E/O transition mudstones

The C_{25} HBI alkenes known as haslenes are produced by few diatom taxa. The genus *Rhizosolenia* produces either C_{25} or C_{30} HBI alkenes, or both. The genera *Haslea*, *Navicula* and *Pleurosigma* produce only C_{25} HBI alkenes (Volkman et al., 1994; Sinninghe Damsté et al., 2004). These components differ in terms of their biosynthesis from the most common acyclic and cyclic isoprenoid natural products because their skeletons are characterized by a distinctive "T branch." These alkenes are prone to sulfurization during sedimentation or early diagenesis (Kohnen et al., 1990; Sinninghe Damsté et al., 2006). Sulfurized C_{25} HBIs can yield C_{25} HBI alkane through desulfurization during diagenesis (Katsumata and Shimoyama, 2001). The C_{25} HBI alkane and C_{25} HBI thiophenes can be formed by the reaction of C_{25} HBI alkene with reduced sulfur during early diagenesis. Sulfurization is a major preservation mechanism for unsaturated or functionalized lipids in sediments (Sinninghe Damsté et al., 2006). HBI alkanes could be more readily preserved than siliceous diatom frustules. The first occurrence of HBI alkanes as a chemical fossil is about 20 million years older than that of classical diatom fossils (Sinninghe Damsté et al., 2004).

Gas chromatograms showing the distribution of C_{25} HBI alkane (2,6,10,14-tetramethyl-7-3-methylpentyl)-pentadecane), C_{25} HBI thiophene I (2-(2'-methylbutyl)-3,5-di-(2'-16'-methylheptyl) thiophene, and total two isomers of C_{25} HBI thiophene II (2,-dimethyl-5-[7'-(2',6',10',14-tetramethylpentadecyl)] thiophene) in mudstones from the Il'pinskii section are shown in Fig. 4 and Table 2. The mass spectra of the C_{25} HBIs permitted their structural identification by comparison with published data (Sinninghe Damsté et al., 1989; Katsumata and Shimoyama, 2001). The relative abundance of the C_{25} HBIs in sedimentary rocks from the Il'pinskii section increases markedly above the E/O boundary. In mudstones from the upper Alugivayam Formation, the major constituent of the hydrocarbon fraction is C_{25} HBIs, including HBI thiophenes I and II (Fig. 4). Stratigraphic variation of HBI alkane and HBI thiophenes show different patterns (Fig. 5). C_{25} HBI alkane concentrations have a maximum value of about 2.56 μg/g TOC, and are highest in samples from the Alugivayam Formation. Concentrations of total two isomers of C_{25} HBI thiophene II, with a maximum value of about 2.53 μg/g TOC (similar to that of C_{25} HBI alkane) show the highest values in mudstones from the uppermost three samples from the Alugivayam Formation. Concentrations of C_{25} HBI thiophene I are very low (<0.51 μg/g TOC). Concentrations of HBI I are highest in mudstones of the Alugivayam Formation and increase gradually above the E/O boundary, together with the other HBIs (Fig. 5).

HBI thiophenes are formed when sulfur is incorporated into C_{25} HBI alkenes during early diagenesis. The incorporation of H_2S sulfur into double-bond structures at the sediment–water interface is well known as the process by which organic sulfur compounds are formed (Sinninghe Damsté et al., 2006). A high abundance of HBI thiophenes, therefore, reflects elevated concentrations of both HBI alkenes and H_2S in the sedimentary environment. Elevated concentrations of both HBI alkanes and HBI thiophenes in mudstones from the uppermost Alugivayam Formation suggest higher production and/or preservation of diatom-derived organic matter under reducing depositional conditions.

According to Sinninghe Damsté et al. (2004), the contribution of diatom-derived C_{25} HBI alkane is accurately reflected by the ratio of HBI alkane to phytane (Ph) derived from all photosynthetic algae and cyanobacteria. Mudstones from the Oligocene Alugivayam Formation have elevated HBI/Ph ratios that range from 0.19 to 4.34 (Table 3). Eocene mudstones have considerably lower HBI/Ph ratios below 0.5 (Table 3). Putting these data into a broader context, the Early Oligocene Menilite Shale in Poland has a HBI/Ph ratio of 3.31

(Sinninghe Damste et al., 2004), which is in the range of HBI/Ph ratios yielded by mudstones from the Oligocene Alugivayam Formation in the present paper.

3.4. Source of HBIs in Oligocene marine mudstones

The paucity of diatom fossils through the E/O transition in the Il'pinskii section is likely due to the unstable nature of diatom frustules. Although Eocene to Oligocene sedimentary rocks in the Il'pinskii section contain very few diatoms, Gladenkov and Gladenkov (2007) found rare examples in mollusk casts and carbonate concretions from the same section; taxa documented include the genus *Cavitatus* (*C.* cf. *jouseanus*) and species *Odontella sawamurae*, but the genus *Rhizosolenia* was absent above the Mulatkhanskii Sandstone beds. The earliest representatives of the genus *Cavitatus* (*C. jouseanus*) appeared in the North Pacific in the early Oligocene (about 31 Ma; Akiba et al., 1993; Gladenkov and Barron, 1995). In high latitudes of the Southern Ocean, the diatom *Rhizosolenia oligocaenica* is a lower Oligocene index fossil

(Baldauf and Barron, 1991; Harwood and Maruyama, 1992). The *R. oligocaenica* Zone is divided in two subzones separated by the first occurrence of *C. jouseanus* at about 31 Ma. The first occurrence of the genus *Cavitatus* corresponds to the upper part of the *R. oligocaenica* Zone in the North Pacific (Gladenkov, 1998, 1999).

The diatom genera *Rhizosolenia, Haslea*, *Navicula*, *Pleurosigma* or their ancestors are considered to be major sources of HBI alkanes and HBI thiophenes (Volkman et al., 1994; Belt et al., 1996, 2000, 2001, 2002; Sinninghe Damsté et al., 1999, 2004). The fossil genus *Rhizosolenia* was globally widespread in the early Oligocene (Baldauf, 1992). In sediment from DSDP Site 138, *Rhizosolenia* represents between 1% and 5% of diatom individuals (Jousé, 1978). In contrast, the fossil genera *Haslea*, *Navicula*, and *Pleurosigma* did not flourish during the E/O transition. The pronounced change in the concentration of HBI biomarkers strongly suggests that *Rhizosolenia* prevailed in the diatom community of the northwest Pacific region after the E/O transition.

3.5. Paleo-oceanographic changes during the E/O transition

n-Alkanes are ubiquitous in the material addressed by this study; their long- and short-chain homologs are known to be derived from higher-plant wax and aquatic organisms, respectively. *n*-Alkanes in Il'pinskii section mudstones are dominated by lower-molecular-weight *n*-alkanes (Table 1). C_{27} to C_{29} steroids biosynthesized by all eukaryotes are also common compounds in the samples. C_{27} and C_{28} steroids are derived predominantly from aquatic phytoplankton and marine zooplankton (Volkman, 1986). The C_{29} steroids are characteristic of higher plants (Huang and Meinschein, 1979), although a microalgal source is also present (Volkman, 1986). The Il'pinskii section material generally contains four dinosteranes (4,23,24-trimethylcholestanes), which are known as dinoflagellate biomarkers. These compounds are four isomers (23S, 24S), (23S, 24R), (23R, 24R), and (23R, 24S), of C_{30} 4α-methyl steranes (Summons et al., 1987). The relative abundance of dinosteranes versus total steranes (C_{27}, C_{28}, and C_{29} regular steranes) indicates the relative contribution of dinoflagellate-derived organic matter to the sediment (discussed below).

Paleo-oceanographic changes recorded in the Il'pinskii section during the E/O transition can be divided into four stages based on the geochemical characteristics of mudstones (Fig. 6). The first stage, corresponding to the Kilakirnun Formation and the lower Gailkhavilanvaym Formation (below the glauconitic sandstone) is characterized by low C/N (<10) and C/S (<1.1) ratios, reflecting the comparatively low contribution of terrestrial organic matter and the presence of an anoxic depositional environment. In the second stage, the terrestrial contribution abruptly increases coincident with the deposition of glauconitic sandstones. The significant increase in the C/S ratio at and above the glauconitic sandstones suggests that the upper Gailkhavilanvaym Formation records the development of a suboxic depositional environment. The upward change in the dinosterane/sterane ratio suggests that the contribution of dinoflagellate-derived organic matter to the sediment decreased through time from the late

Eocene to the Oligocene.

The third stage, corresponding to the lower Alugivayam Formation, is near and above the E/O boundary. This stage is characterized by a remarkably high C/S ratio (2 to 10), a low C/N ratio (<10), and an abrupt increase in HBI alkane concentration. The timing of the increase in diatom-derived HBI alkane in mudstones (above sample ILP-75) corresponds to the abrupt increase in the C/S ratio. The high C/S ratio in the lower part of the Alugivayam Formation reflects the abrupt formation of oxic bottom water, which is supported by the abundance of mollusks at the same level (Fig. 2).

The C/N and C/S ratios of mudstones from the Upper Alugivayam Formation are similar to those of the first stage (below the glauconitic sandstones). This final stage is characterized by the highest HBI alkane and HBI thiophene concentrations and the lowest dinosterane/sterane ratios, indicating a large contribution from diatom-derived organic matter and an anoxic depositional environment. The incorporation of sulfur into HBI alkenes to form HBI thiophenes proceeds rapidly under reducing, H_2S-rich conditions (Sinninghe Damsté et al., 2006). The high concentrations of HBI thiophenes supports the inference of an anoxic depositional environment as indicated by the low C/S ratios (<1.0). HBI thiophene II is generally more abundant than HBI thiophene I, suggesting that the HBI thiophene II is more readily formed during early diagenesis. The highest concentration of total HBI compounds and the lowest dinosterane/sterane ratio in the fourth stage indicate an increased proportion of HBI-producing diatoms in the planktonic community (Fig. 6).

In the Ceara Rise region of the western equatorial Atlantic, the accumulation of biogenic silica abruptly increased during the early Oligocene, possibly in response to increased diatom production due to global cooling (Mikkelsen and Barron, 1997). In the Il'pinskii section, however, stratigraphic variation in SiO_2 content is muted, even though the concentration of HBI diatom biomarkers increased with the passage of time. The preservation of biogenic silica in marine sediment is controlled by the surface area and surface characteristics of diatom tests, and the degree of amorphous biogenic silica saturation in seawater and pore water. The SiO_2 concentration of mudstones from the Il'pinskii section is generally less then 70%, reflecting a small contribution of biogenic silica to the seafloor. A low concentration of amorphous silica in the water column and sediment and/or the unstable nature of diatom frustules may have caused dissolution of siliceous diatom tests. Our present findings, however, indicate that biogenic silica preservation in sediment is not essential in the evaluation of diatom productivity because their biomarkers can be used instead. In the material studied, a major change in the concentration of HBIs suggests that diatoms gradually became the main primary producer in the northwest Pacific region after the E/O transition.

Considerable amounts of diatom biomarkers are present in mudstones below and close to the Mulatkhanskii Sandstones. The abrupt increase in HBI concentration in these strata may reflect an abrupt climatic cooling event during the E/O transition, as was documented at the Ceara Rise in the equatorial Atlantic. The presence of HBIs in sedimentary rocks that record the E/O transition may reflect the appearance of the Oligocene marine diatom *R. oligocaenica*. In the Il'pinskii section, the lowest part of the *R. oligocaenica* Zone can be located between ILP-75 and ILP-75.5. According to the Baldauf and Barron (1991), the E/O boundary would be located below the *R. oligocaenica* Zone. The E/O boundary in the Il'pinskii section, therefore, can be located below and close to the Mulatkhanskii Sandstones as is the case of the Ceara Rise in the equatorial Atlantic. The abrupt formation of oxic bottom water recorded by an increased C/S ratio may reflect abrupt climatic cooling during the E/O transition. Our present results demonstrate the utility of HBIs as biomarkers for regional biostratigraphic correlation in the northwest Pacific during the E/O transition.

4. Conclusions

Rapid global lowering of atmospheric and oceanic temperatures initiated the formation and expansion of polar ice sheets during the E/O transition. Dramatic changes in diatom communities and a large increase in diatom community diversity took place through the E/O transition. The diatom record through the E/O transition in the northwest Pacific is poor, however, owing to poor preservation of siliceous diatom tests. HBIs, which are diatom biomarkers, are present in sedimentary rocks from the Il'pinskii section, Kamchatka Peninsula, which exposes Eocene to Oligocene strata containing the E/O boundary.

Diatom biomarkers such as C_{25} HBI alkanes and C_{25} HBI thiophenes are common in mudstones from the Il'pinskii section. Concentrations of these diatom biomarkers in Oligocene mudstones are clearly higher than those in Eocene mudstones. HBIs increase abruptly above the E/O boundary, whereas dinosteranes, the dinoflagellate-specific biomarkers, decrease gradually from the Eocene to the Oligocene. This suggests that diatoms gradually became the dominant primary producers in the northwest Pacific region throughout this interval. Paleo-oceanographic changes in the Il'pinskii region through the E/O transition can be divided into four stages based on stratigraphic changes in C/N ratio, C/S ratio, and concentrations of

HBI alkane and HBI thiophenes. In addition to the abrupt increase in diatom biomarker concentrations, the E/O boundary is also characterized by the abrupt formation of suboxic to oxic bottom ocean water, which may reflect a change in ocean circulation due to rapid global cooling during the E/O transition. A position for the E/O boundary in the Il'pinskii section is proposed based on stratigraphic changes in depositional environment and on the abundance of HBIs. Poor preservation of siliceous diatom tests in marine mudstones of the E/O transition in the northwest Pacific region may be due to dissolution during settling and early diagenesis. The high concentration of HBIs in these mudstones may represent biogeochemical evidence for the appearance of the Oligocene diatom, the genus *Rhizosolenia*. Finally, HBIs may be useful as biomarkers in regional biostratigraphic correlation during the E/O transition, particularly in the northwestern Pacific.

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Figure Captions

Fig. 1. Location of the study area on the Kamchatka Peninsula.

Fig. 2. Schematic stratigraphic and lithologic sections of the Il’pinskii area. Numbers adjacent to the column indicate sample locations.

Fig. 3. Stratigraphic variation in total organic carbon (TOC) concentration, total sulfur (TS) concentration, TOC/total nitrogen (C/N) ratio, and TOC/Total S (C/S) ratio of Eocene to Oligocene mudstones from the Il’pinskii area. M.S.: Mulatkhanskii Sandstones; L.T.: Laperalamskii tuff; GL: Glauconitic sandstones; dark-shaded areas in stratigraphic column: tuff; light-shaded areas in stratigraphic column: mudstone.

Fig. 4. Partial total ion current chromatograms for hydrocarbon fractions from Ilpinskii

mudstones. Pr: pristane; Ph: phytane; C_{25} HBI alkane: 2,6,10,14-tetramethyl-7-(3-methylpentyl)-pentadecane; C_{25} HBI thiophene I: 2-(2'-methylbutyl)-3,5-di-(2'-16'-methylheptyl)thiophene; C_{25} HBI thiophene II: two isomers of 2,3-dimethyl-5-[7'-(2',6',10'14'-tetramethylpentadecyl)]thiophene; ∗: inner standard, *n*-tetracosane-*d* 50. Number in the figure shows the carbon number of the *n*-alkane.

Fig. 5. Stratigraphic variation in concentrations of C_{25} HBI alkane (2,6,10,14-tetramethyl-7-(3-methylpentyl)-pentadecane), C_{25} HBI thiophene I (2-(2'-methylbutyl)-3,5-di-(2'-16'-methylheptyl) thiophene, and C_{25} HBI thiophene II (Σ two isomers of 2,3-dimethyl-5-[7'-(2',6',10',14-tetramethylpentadecyl)] thiophene) and dinosterane/sterane ratio for the Il'pinskii section. The dinosterane/sterane ratio is based on the mass chromatograms of m/z 231 (Σ four isomers of 4,3,24-trimethylcholestanes) and m/z 217 (Σ (αααR-C_{27}-αααR-C_{29})). M.S.: Mulatkhanskii Sandstones; L.T.: Laperalamskii tuff; GL:

glauconitic sandstones; dark-shaded areas in stratigraphic column: tuff; light-shaded areas in stratigraphic column: mudstone.

Fig. 6. Schematic paleo-oceanographic changes during the Eocene-Oligocene transition. M.S.: Mulatkhanskii Sandstones; L.T.: Laperalamskii tuff; GL: glauconitic sandstones; dark-shaded areas in stratigraphic column: tuff; light-shaded areas in stratigraphic column: mudstone.