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Variations of Mass Accumulation Rates of Long Chain n-alkanes in the Northern North Pacific During the Last 350 kyrs

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ABSTRACT

Land plant waxes preserved in the marine sediments are considered to be a useful proxy to reconstruct the terrestrial palaeoenvironments. Long chain n-alkanes were analysed to understand the historical variations of the supply of terrigenous organic matter during the last 350 kyrs. Results show that the mass accumulation rates (MARs) of the long chain n-alkanes tended to increase during glacial stages particularly during the last glacial period in the Emperor Seamount area of the northern North Pacific Ocean. Simultaneous increases in the amount of organic matter attached to eolian dust could have resulted in increased MARs of terrestrial organic matter during glacial stages (marine isotopic stages 2, 4, and 6). In contrast, decrease of aridity along with moderate westerly winds during the interglacial periods resulted in a lower rate of dust production and thus reduced transport of terrestrial organic matter towards the northern North Pacific Ocean.

Keywords: Long chain n-alkanes, Terrestrial organic matter, Northern North Pacific Ocean, Emperor Seamount, Mass accumulation rates

INTRODUCTION

The analysis of molecular biomarkers in deep-sea sediments has become a very valuable tool for the reconstruction of palaeoclimate changes over the Quaternary. Marine sediments contain organic matter derived from both terrestrial and marine organisms. Higher molecular weight n-alkanes and fatty acids significantly detected in pelagic sediments are considered as terrestrial organic matter derived from higher land plants [1, 2]. Homologous series of long-chain n-alkanes are typical lipids that are abundant constituents of terrestrial higher plant epicuticular waxes [3]. These terrestrial organic compounds in pelagic sediments can provide us useful information on terrestrial environmental changes.

The non-functionalised n-alkanes are relatively refractory compounds. Hence, they probably constitute the best biomarkers to understand the terrestrial influences in the North Pacific Ocean in the past.

The present study is focused on the relationships between variation of the mass accumulation rates (MARs) of land plant n-alkanes and the glacial/interglacial changes during these 350 kyrs. Organic matter was extracted from these sediments and analysed for land plant n-alkanes. This study provides an insight for terrestrial palaeoenvironmental changes with respect to glacial/interglacial changes in the northern areas of Asia.
Sampling and Core Description
Sampling was carried out during the Cruise KH99-3 the R/V Hakuho Maru. A piston core sample collected from the Emperor Seamount of the northern North Pacific Ocean (ES core) is used for the present study (Fig. 1). Core was approximately 8.5 m long and consisted of clay, silty clay, calcareous clay and diatomaceous clay intercalated with several volcanic ash layers. This core was cut into several vertical sections and distributed among onboard scientists for multidisciplinary research including our studies of organic geochemistry and magnetic susceptibility. Samples were stored in stainless steel cases under —20°C and carried to laboratory, cut again into 5-cm sections, freeze dried, ground into approximately under 200-mesh size, and used for biomarker analysis.

Lipid Analysis
After the addition of C24D50 and C30D62 internal standards (iSTD), approximately 5g of pulverized sample from each sediment section was ultrasonically extracted with dichloromethane/methanol (9 : 1) as solvent. Sediments were extracted for three times (using total 100 ml of solvent) and all aliquots were combined before evaporating completely using rotary evaporator. The n-alkanes were separated by silica gel (60N, 63-210 µm) column chromatography with hexane. They were analysed by gas chromatography (GC) and gas chromatography — mass spectrometry (GC-MS).

The n-alkanes were analysed using Hewlett Packard HP6890/5973 GC-MS (splitless injection system) equipped with fused silica column (HP-5 MS, 30 m x 0.25 mm). GC was programmed isothermally at 40°C for 2 min., from 40°C to 300°C at 4°C/min. and held at 300°C isothermally for 25 minutes for n-alkanes. Concentrations of n-alkanes were determined based on internal standards.

Dating
Age model for ES core was developed based on peak to peak correlation of magnetic susceptibilities and δ¹⁸O data of the ES core to the nearby ODP core (Site 883) and its age model [4].

RESULTS
Bulk Properties of Core Sediments
Magnetic susceptibility and the δ¹⁸O profiles show that the ES core, approximately 8.5 m long, has a sedimentation history over 350 kyrs covering almost nine glacial/interglacial periods [5, 6]. The sediments are mostly composed of clay and silt with intercalations of diatomaceous and calcareous clays along with several water-laid volcanic ash layers. Total organic carbon (TOC) contents are relatively low (< 1%) throughout the core.

Relative Distribution of n-alkanes
The distribution and the abundance of a mass fragmentogram of n-alkanes (m/z = 57) obtained from the GC-MS analysis of ES core is shown in Fig. 2. All the chromatograms, throughout the core, show a similar distribution pattern characterized by uni-modal distribution maximising at n-C27, n-C29 or n-C31. Carbon numbers range from n-C17 to n-C35 and with prominent peaks of n-alkanes at n-C27, n-C29 and n-C31 while n-C17 and n-C19 alkanes are at a low concentration. n-Alkanes having more than 23 carbons are generally abundant compared to those with
fewer carbons. Carbon preference index (CPI) values of ES core range from 1.4 to 4.5 with an average value of 3.1. However, CPI values do not vary significantly with glacial/interglacial changes.

**MARs (µg cm⁻² kyr⁻¹) of Long Chain n-alkanes (C_{27}, C_{29}, C_{31})**

MAR of long chain n-alkanes was approximately two fold higher during the last glacial period (Fig. 3) compared to the present interglacial period at the northern North Pacific Ocean core site. MAR was as low as 0.192 µg cm⁻² kyr⁻¹ during the Holocene, started to increase from approximately 10,000 yrs ago and maximized to 1.0 µg cm⁻² kyr⁻¹ at the last glacial maximum (16,000 kyrs). Again MAR slightly increased during marine isotopic stages (MIS) 4, 6 and 8, while during MIS 5, 7 and 9 had slightly decreased trends. Average MARs for the last 5 glacial/interglacial stages were 0.19 (MIS1), 0.63 (MIS2), 0.24 (MIS3), 0.23(MIS4), and 0.15 µg cm⁻² kyr⁻¹ (MIS5).

**DISCUSSION**

Lower abundance of the shorter chain n-alkanes (C_{17} and n-C_{18}) in the ES core sediments (Fig. 2) indicated minor contribution of marine source (algae and planktons) organic matter [7], whereas greater abundance of the long chain n-alkanes (C_{27}, C_{29}, and C_{31}) indicated major contribution of land plant source [7, 8] to the northern North Pacific Ocean. The higher CPI values, which indicate the odd carbon predominance of n-alkanes (Fig. 2), were also in accordance with abundant land-derived organic matter [9]. In vascular plant epicuticular waxes, the typical n-alkane CPI values range from 4–10 [8, 10]. In contrast, CPI values in marine bacteria and algae which contain less than C_{20} alkanes range only from about 1 to 1.5 [11] n-Alkanes in anthropogenic and naturally derived petroleum/kerogen and pyrolytic sources show no odd/even predominance [12]. The CPI of the terrestrial end member in marine aerosols has been estimated to be about 5–10 [3]. Hence, the present CPI values indicated mixture of both marine and terrestrial source. However, CPI could change with increasing maturity [9], which was insignificant for these sedimentary cores since they were shallow, and had been subjected only to early digenetic modifications. Long to short chain ratio (H/L) of n-alkanes indicates relative abundance of terrestrial to marine source organic matter [12]. These core sediments have very high H/L ratios (average 13.3), probably due to preferential loss of short chain n-alkanes, as in the case of lacustrine sediments in Lake Haruna, Japan [13]. Abnormally high H/L ratios (>100) should definitely be influenced by the selective loss of short chain n-alkanes rather than greater contents of terrestrial organic matter. Both H/L ratio and CPI values do not show significant glacial/interglacial time series changes.

MARs of long chain n-alkanes of ES core show major increase during MIS 2 with a relatively smaller increase during MIS 4, 6 and 8, whereas MARs during MIS 1, 3, 5 and 9 show decreased values (Fig. 3). These terrestrial waxes were recorded more than twice as much during the last glacial maximum compared to the present interglacial period. The terrigenous materials had to be transported to this core site only by the deposition via atmosphere, because river could hardly supply organic matter to this remote seamount area. Increased MARs of land plant waxes during glacial periods,
MIS 2, 4, 6 and 8 signify diminished precipitation over the Asian continent during the summer monsoon period and strengthened westerly winds. Increases in the amount of terrestrial organic matter attached to eolian dust could have led to increased MARs of terrestrial supply during MIS 2, 4, and 6 whereas decrease of aridity and moderate westerly winds during the interglacial periods resulted poor dust influx and thus weakened terrestrial organic matter transportation towards the northern North Pacific Ocean. These results are consistent with the studies [14, 15] on terrestrial organic carbon and long chain n-alkanes from the north-western Pacific Ocean core sediments. Therefore, we conclude that the most likely source of terrestrial supply during the glacial periods was eolian dust, mainly from the northern areas of Asian continent.

CONCLUSION

Present study shows greater MARs of terrestrial derived long chain n-alkanes during glacial stages whereas lower MARs during interglacial periods in the Emperor Seamount site of the North Pacific Ocean. The results are consistent with those in the recorded Western North Pacific Ocean core sediments and provide strong evidence of westerly wind influence even at the northernmost Pacific Ocean areas.

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