Reconstruction of paleoproductivity in the Sea of Okhotsk over the last 30 kyr

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[1]   Marine- and terrestrial-derived biomarkers (alkenones, brassicasterol, dinosterol, and long-chain *n*-alkanes), as well as carbonate, biogenic opal, and ice-rafted debris (IRD), were measured in two sediment cores in the Sea of Okhotsk, which is located in the northwestern Pacific rim and characterized by high primary productivity. Down-core profiles of phytoplankton markers suggest that primary productivity abruptly increased during the global Meltwater Pulse events 1A (about 14 ka) and 1B (about 11 ka) and stayed high in the Holocene. Spatial and temporal distributions of the phytoplankton productivity were found to be consistent with changes in the reconstructed sea ice distribution on the basis of the IRD. This demonstrates that the progress and retreat of sea ice regulated primary productivity in the Sea of Okhotsk with minimum productivity during the glacial period. The mass accumulation rates of alkenones, $CaCO_3$, and biogenic opal indicate that the dominant phytoplankton species during deglaciation was the coccolithophorid, *Emiliania huxleyi*, which was replaced by diatoms in the late Holocene. Such a phytoplankton succession was probably caused by an increase in silicate supply to the euphotic layer, possibly associated with a change in surface hydrography and/or linked to enhanced upwelling of North Pacific Deep Water.   *INDEX TERMS:* 1050 Geochemistry: Marine geochemistry (4835, 4850); 1055 Geochemistry: Organic geochemistry; 4267 Oceanography: General: Paleoceanography; *KEYWORDS:* Okhotsk Sea, paleoproductivity, sediment

1. Introduction

[2] The subarctic North Pacific, including the Sea of Okhotsk and Bering Sea, is the silica-type high-productivity ocean [*Honda et al.*, 1997a, 1997b; *Honjo*, 1997; *Takahashi et al.*, 1997, 2000]. The biological pump in this region of the ocean works more efficiently to enhance the uptake of atmospheric CO_2 [*Honda et al.*, 2002], and the subarctic North Pacific is hence thought to play an important role in the global carbon cycle and global climate change [*Wong et al.*, 1995; *Takahashi*, 1998]. Despite its importance, this region is one of the least studied in the oceans because the water depth in most areas is deeper than the calcite lysocline depth and shells of calcaceous plankton, which can be used for conventional dating (oxygen isotope and radiocarbon chronostratrigraphy using foraminiferal shells), are not preserved in the sediments.

[3] Organic carbon, $CaCO_3$, and biogenic opal contents in marine sediments have been used as key parameters to assess paleoproductivity [*Prahl et al.*, 1989; *Berger et al.*, 1989; *Mortlock et al.*, 1991; *Simmield et al.*, 1994]. Previous paleoceanographic studies in the subarctic regions of the North Pacific have consistently indicated that productivity in this regions was depressed in the last glacial period and increased during deglaciation [*Keigwin et al.*, 1992; *Nakatsuka et al.*, 1995; *Gorbarenko*, 1996; *Narita et al.*, 2002; *Ternois et al.*, 2001; *Gorbarenko et al.*, 2002a], except for the northeastern sector [*Zahn et al.*, 1991]. These studies have also shown that the variation pattern of biogenic opal content differed significantly from that of $CaCO_3$, suggesting a dramatic change in the dominant plankton species from the deglacial to the present [*Keigwin et al.*, 1992; *Gorbarenko*, 1996; *Gorbarenko et al.*, 2002a].

[4] Despite these first-order interpretations, the variations in coccolithophorid productivity between glacial and interglacial periods in the high-latitude North Pacific have remained unclear because carbonate preservation is influenced by changes in pore water chemistry at the sediment-water interface [*Emerson and Bender*, 1981; *Archer*, 1991; *Broecker et al.*, 1991]. In fact, $CaCO_3$ dissolution in the southern Okhotsk Sea sediments has varied strongly [*Gorbarenko et al.*, 2002a]. In contrast, C_{37}-C_{39} alkenones derived from some Haptophyceae, such as the coccolithophores *Emiliania huxleyi* (*E. huxleyi*) and *Gephyrocapsa oceanica* (*G. oceanica*) [*Marlowe et al.*, 1984; *Conte et al.*, 1994], are one of the most refractory lipids against the

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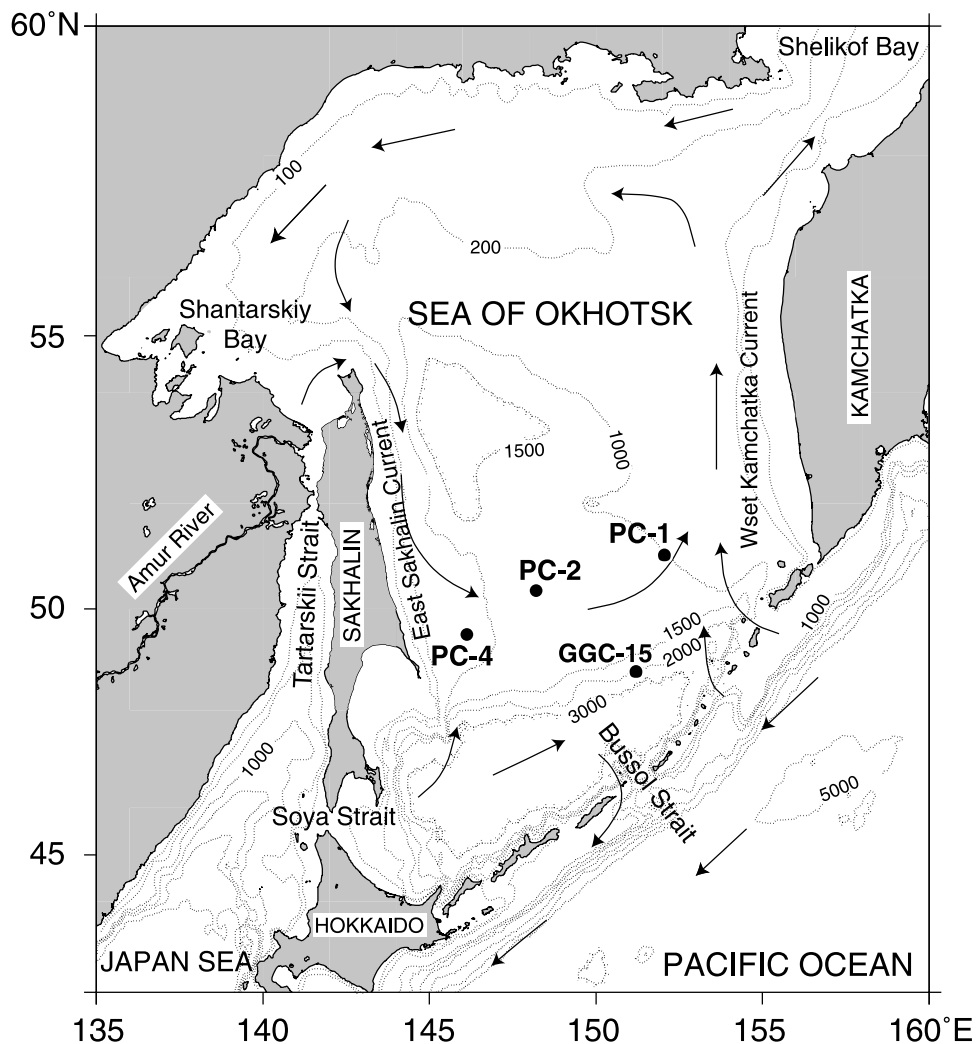
Figure 1. Bathymetric map of the Southern Okhotsk Sea showing the locations of PC-1, PC-2, PC-4, and GGC-15 sediment cores. Arrows show the directions of major surface currents.

effects of biodegradation and diagenesis [*Rechka and Maxwell*, 1988; *Sun and Wakeham*, 1994]. Thus concentration and mass accumulation rates (MAR) of alkenones in sediment cores can be better used as an indicator of coccolithophore productivity in the past.

[5] The Sea of Okhotsk is located along the northwestern Pacific rim and is one of the largest marginal seas in the world's ocean. Because the sea is a source region for North Pacific Intermediate Water (NPIW) [*Talley*, 1991; *Freeland et al.*, 1998], it is considered to act as an important atmospheric CO_2 sink through a biological pump [*Honjo*, 1996, 1997]. Previous study of a sediment core taken from the southern Okhotsk Sea suggested that changes in the sea ice regime during glacial-interglacial cycles played an important role in controlling biological productivity in the subarctic regions [*Ternois et al.*, 2001]. However, this core site is located far to the south in an area free from seasonal sea ice that is an important characteristic of the modern sea.

[6] In this study, we analyzed three sediment cores taken along a west to east transect in the Sea of Okhotsk for marine and terrestrial biomarkers, including C_{37} alkenones,

dinosterol, brassicasterol, and high molecular weight (HMW) n-alkanes together with bulk biogenic components (TOC, $CaCO_3$, and biogenic opal) and ice-rafted debris (IRD). Here we discuss (1) detailed changes in the paleo-productivity of specific algae and (2) the linkage between paleoproductivity and terrestrial inputs as well as sea ice and other physical characteristics of the Sea of Okhotsk over the last 30 kyr.

2. Oceanographic Setting

[7] The Sea of Okhotsk is separated from the Pacific Ocean by the Kuril Islands and rimmed by the Siberian plain and island of Sakhalin (Figure 1). The Okhotsk Sea connects to the Japan Sea by the Soya and Tartarskii Straits. This sea has a general cyclonic current system with peculiar conditions of water exchange with the North Pacific. Northward water transport (West Kamchatka Current) dominates to the west of the Kamchatka Peninsula, whereas southward transport (East Sakhalin Current) does so to the east of Sakhalin [*Alfultis and Martin*, 1987]. The Okhotsk

Sea marks the southern boundary region of seasonal sea ice. Because of brine rejection by sea ice generation in winter, and subsequent formation of cold and saline water, ventilation of the intermediate water occurs in the sea. During sea ice formation over the northwestern continental shelf, cold brine water, the so-called dense shelf water (DSW), is rejected and sinks to the bottom of the shelf [*Martin et al.*, 1998; *Gladyshev et al.*, 2000]. This DSW exists at around 300–400 m depth and spreads to the south along the Sakhalin coast through the East Sakhalin Current. The volume of outflow of the intermediate water mass from the continental shelf to the southern deep basin has been estimated to be as high as 0.5 Sv [*Gladyshev et al.*, 2000]. This intermediate water mass further penetrates into the North Pacific through the Bussol Strait. Hence the Sea of Okhotsk is the source region of NPIW [*Talley*, 1991; *Wong et al.*, 1995]. The mouth of the Amur River, which is one of the largest rivers in east Siberia, is located adjacent to the northwestern continental shelf of the sea. The water discharge from the Amur River (about 310 km^3 yr^{-1}) [*Vörösmarty et al.*, 1998] also plays an important role in sea ice formation and in the productivity of the Sea of Okhotsk.

[8] The intermediate water formed over the northwestern continental shelf plays an important role in the effective transport of particle matter from the shelf to the open ocean owing to strong tidal mixing and brine rejection by sea ice over the continental shelf [*Nakatsuka et al.*, 2002]. Hence sedimentary components including organic matter to the eastern side of Sakhalin (PC-4 site) should be influenced by lateral transport of particles from the northwestern continental shelf. However, the lateral input of organic matter is not nearly as important as it is for lithogenic particles (T. Nakatsuka et al., unpublished manuscript, 2003) and lateral transport of marine-derived biomarkers are quite a bit less than in situ export production (O. Seki et al., manuscript in preparation, 2004).

3. Material and Methods

[9] Three piston cores: XP98-PC-1 (location 51°00′N 152°00′E, water depth 1107 m), PC-2 (location 50°24′N 148°20′E, water depth 1258 m), and PC-4 (location 49°30′N 146°07′E, water depth 664 m) were obtained along an east-west transect in the central Sea of Okhotsk during XP-98 cruise by the R/V *Professor Khromov* as part of a joint Japanese-Russian-U.S. program.

[10] Total organic carbon (TOC) contents were determined using a Fisons NA 1500 CHN analyzer after the treatment of sediment samples (15–20 mg) to remove calcium carbonate. Total carbon (TC) contents were also determined using a Fisons NA 1500 CHN analyzer. The analytical error based on triplicate analyses was within 7%. Contents of CaCO$_3$ were calculated using the following equation:

$$CaCO_3 = (TC - TOC) \times 8.34. \qquad (1)$$

[11] The δ^{13}C analysis of bulk organic matter was conducted with a Finnigan-MAT Delta Plus isotope ratio mass spectrometer interfaced to a Fisons NA 1500 CNS analyzer.

Values were corrected for the procedural blanks and expressed in δ^{13}C$_{org}$ units relative to the standard PeeDee belemnite (PDB). Analytical errors (reproducibility) of TOC and δ^{13}C$_{org}$ measurements were within 1% and 0.2‰, respectively. Biogenic opal contents were determined after extraction with an alkaline solution [*Mortlock and Froelich*, 1989]. The coarse (>63 μm) fraction of terrigenous grains was analyzed with a laser diffraction grain size analyzer (Coulter LS230) after removing organic carbon, biogenic carbonate, and biogenic opal by hydrogen peroxide, hydrochloric acid, and sodium carbonate solutions, respectively.

[12] Total lipids were extracted from the dried sediments (2–4 g) with dichloromethane/methanol (95:5) using an accelerated solvent extractor (Dionex: ASE 200) at 100°C and 1000 psi for 15 min. It has been well established that extraction of lipid biomarkers from environmental samples using accelerated solvent extraction is comparable to conventional methods [*Macnaughton et al.*, 1997; *Richter*, 2000]. The extracts were concentrated and then saponified with 1.0 M KOH/methanol. Neutral components were isolated by extraction with *n*-hexane/dichloromethane (10:1) and were further separated into two subfractions by silica gel column chromatography with a modification of *Kawamura* [1995]. Aliphatic hydrocarbons, polynuclear aromatic hydrocarbons, ketones, and aldehydes were eluted with dichloromethane, whereas *n*-fatty alcohols plus sterols were eluted with dichloromethane/methanol (95:5).

[13] Lipid class compounds (*n*-alkanes, alkenones, and sterols) were analyzed with a HP6890 GC equipped with an on-column injector, CPSIL-5 CB fused silica capillary column (60 m × 0.32 mm inner diameter, film thickness of 0.25 μm), and flame ionization detector. The GC oven temperature was programmed from 50°C to 120°C at 30°C/min and then 120°C to 310°C at 5°C/min. The identification of each compound was achieved by GC/mass spectrometry. For the quantification of ketones and aliphatic hydrocarbons, an internal standard (C$_{24}$D$_{50}$ *n*-alkane) was added to the subfractions before the injection to the GC. Recoveries of *n*-alkanes (C$_{29}$ and C$_{32}$) were >90%. Duplicate analyses of the sediments showed that reproducibility for the lipids is better than 90%. Blank experiments performed in parallel with sample analysis showed no detectable peaks on the GC trace.

4. Results

4.1. Age Models

[14] The age models for the XP98-PC cores are described in the work of M. Ikehara et al. Paleoenvironmental changes in the Sea of Okhotsk during the late Quaternary inferred from sedimentary properties and stable isotopes in foraminiferas, submitted to *Quaternary Research*, 2003, hereinafter referred to as Ikehara et al., submitted manuscript, 2003), though the relevant age control points and dating methods are presented in Table 1. Age models for PC-1 and PC-2 were determined by accelerator mass spectrometer-radiocarbon (AMS-^{14}C) dates using shells of planktonic foraminifera in the upper part of the sequence and correlation of benthic foraminiferal δ^{18}O profiles in the Okhotsk Sea sediments with the δ^{18}O curve of *Martinson et al.* [1987] in the lower part of the sequence (see Figure 2a). AMS ^{14}C

Table 1. Age Control Points and Dating Methods for Cores PC-1, PC-2, and PC-4

PC-4				PC-2				PC-1			
Depth, cm	Events	Age, kyr	LSR,[a] cm kyr^{-1}	Depth, cm	Events	Age, kyr	LSR, cm kyr^{-1}	Depth, cm	Events	Age, kyr	LSR, cm kyr^{-1}
0	core top	0.00		0	core top	0.00		0.0	V34-98[b]	2.50	
			37.5				24.1				17.4
138.4	MS1[c]	3.69		11.1	AMS[d]	0.46		63.4	AMS	6.11	
			16.8				19.2				13.2
232.9	MS2	9.31		39.5	AMS	1.94		122.2	AMS	10.55	
			10.7				19.7				7.7
289.7	MS3	14.62		81.4	AMS	4.07		213.1	AMS	22.43	
			8.3				17.7				6.9
382.8	MS4	25.89		103.6	AMS	5.32		404.0	MIS[e] 3.3	50.21	
			9.7				15.8				8.0
570.1	MS5	45.10		189.2	AMS	10.83		474.1	MIS 4.0	58.96	
			14.0				7.5				9.1
872.7	MS6	66.70		214.1	AMS	14.14		609.6	MIS 5.0	73.91	
			17.0				7.8				12.3
1065.0	MS7	77.98		368.6	MIS 3.1x	33.83		675.5	MIS 5.1	79.25	
							3.0				7.3
				385.9	Ash-A	39.59		821.8	MIS 5.3	99.38	
							10.4				7.4
				496.2	MIS 3.3	50.21		994.3	MIS 5.51	122.56	
							11.9				
				777.3	MIS 5.0	73.91					
							12.0				
				924.6	MIS 5.1x	86.19					

[a]LSR, linear sedimentation rate.
[b]V34-98, age was estimated by comparison of $\delta^{18}O$ and $\delta^{13}C$ of foraminifera to those of V34-98 [*Gorbarenko et al.*, 2002a, 2002b].
[c]MIS, ages were estimated by marine isotope stage events.
[d]AMS, ^{14}C ages by accelerator mass spectrometer.
[e]MS, ages were estimated by comparison of magnetic susceptibility to that of PC2.

ages were obtained after calibration of $\delta^{13}C$ using CALIB software [*Stuiver et al.*, 1998]. In this calibration we assumed a reservoir effect of ^{14}C in the Sea of Okhotsk of 950 years [*Keigwin*, 1998]. Core PC-2 is well dated by ^{14}C analyses for the last 14 kyr. The number of dates for PC-1 is more limited because of the low contents of foraminifera shells recovered. Unfortunately, carbonate contents in PC-4 were also quite low. Hence an age model for PC-4 was determined by comparison of magnetic susceptibility with that of PC-2 (see Figure 2b). Magnetostratigraphy in Okhotsk Sea sediments during the late Quaternary has been well developed by *Gorbarenko et al.* [2002b]. Down-core profiles of magnetic susceptibility in PC-2 and PC-4 are similar to those of *Gorbarenko et al.* [2002b]. Figure 3 shows the age versus depth profiles of the three sediment cores.

4.2. Total Organic Carbon, C/N, and $\delta^{13}C_{org}$

[15] The C/N ratio and $\delta^{13}C_{org}$ can be used to evaluate the relative sources of sedimentary materials [*Eadie and Jeffrey*, 1973]. The C/N ratio and $\delta^{13}C_{org}$ values in the three cores range from 6.3 to 9.3 and from -23.7 to -20.5‰, respectively [*Seki et al.*, 2003] and their variation patterns are similar to those of GGC-15 [*Ternois et al.*, 2001]. It is well known that marine algae typically have C/N ratios between 4 and 10, while C/N ratios of vascular land plants are greater than 20 [*Meyers*, 1994]. Thus the organic carbon preserved in the sediments is mainly of marine origin. However, the deglacial period (17-6 ka) was characterized by lighter $\delta^{13}C_{org}$ values and higher C/N ratios, suggesting

an enhanced contribution of terrigenous organic matter to the sediments during deglaciation. A deglacial increase in the contribution of terrestrial organic matter was also recognized in the historical profiles of terrestrial biomarkers (Figures 4h, 5i, and 6h). The deglacial increase was found to be caused by submergence of the land shelf during the deglaciation [*Seki et al.*, 2003].

[16] Figures 4−6 show down-core profiles of $\delta^{18}O$, TOC, opal, $CaCO_3$, IRD, and specific biomarkers in cores PC-1, PC-2, and PC-4 plotted against calendar age over the last 30 kyr. The XP-PC cores show that TOC contents were low before 16 ka but increased between 15 and 6 ka and stayed high throughout the Holocene (Figures 4b, 5b, and 6a). Two TOC peaks were recognized at 15 and 10 ka in PC-1 and at 14 and 11 ka in PC-2, but there is no peak in PC-4 during the deglacial period. This result indicates that marine productivity abruptly increased during the deglacial period in the eastern Okhotsk Sea and remained high during the Holocene in the whole Okhotsk Sea. AMS-^{14}C analyses in PC-2 indicate that the deglacial peaks of TOC are, within dating error, coeval with global meltwater pulses (MWP) 1A and 1B as proposed by *Fairbanks* [1989], and as previously identified in the Southern Okhotsk Sea [*Gorbarenko et al.*, 2002a]. The drop in TOC contents between MWP 1A and 1B probably corresponds to the Younger Dryas event.
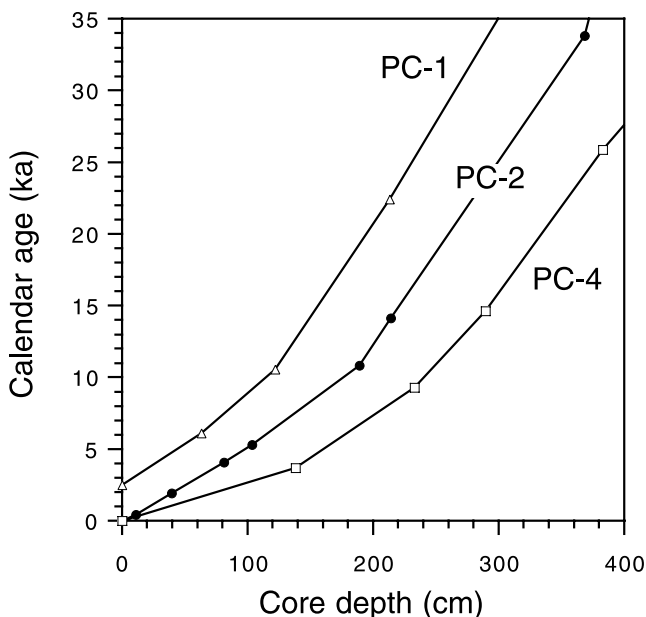
4.3. Carbonate and Biogenic Opal

[17] The $CaCO_3$ contents in cores PC-1 and PC-2 are quite low before 16 ka and then show a sudden and abrupt
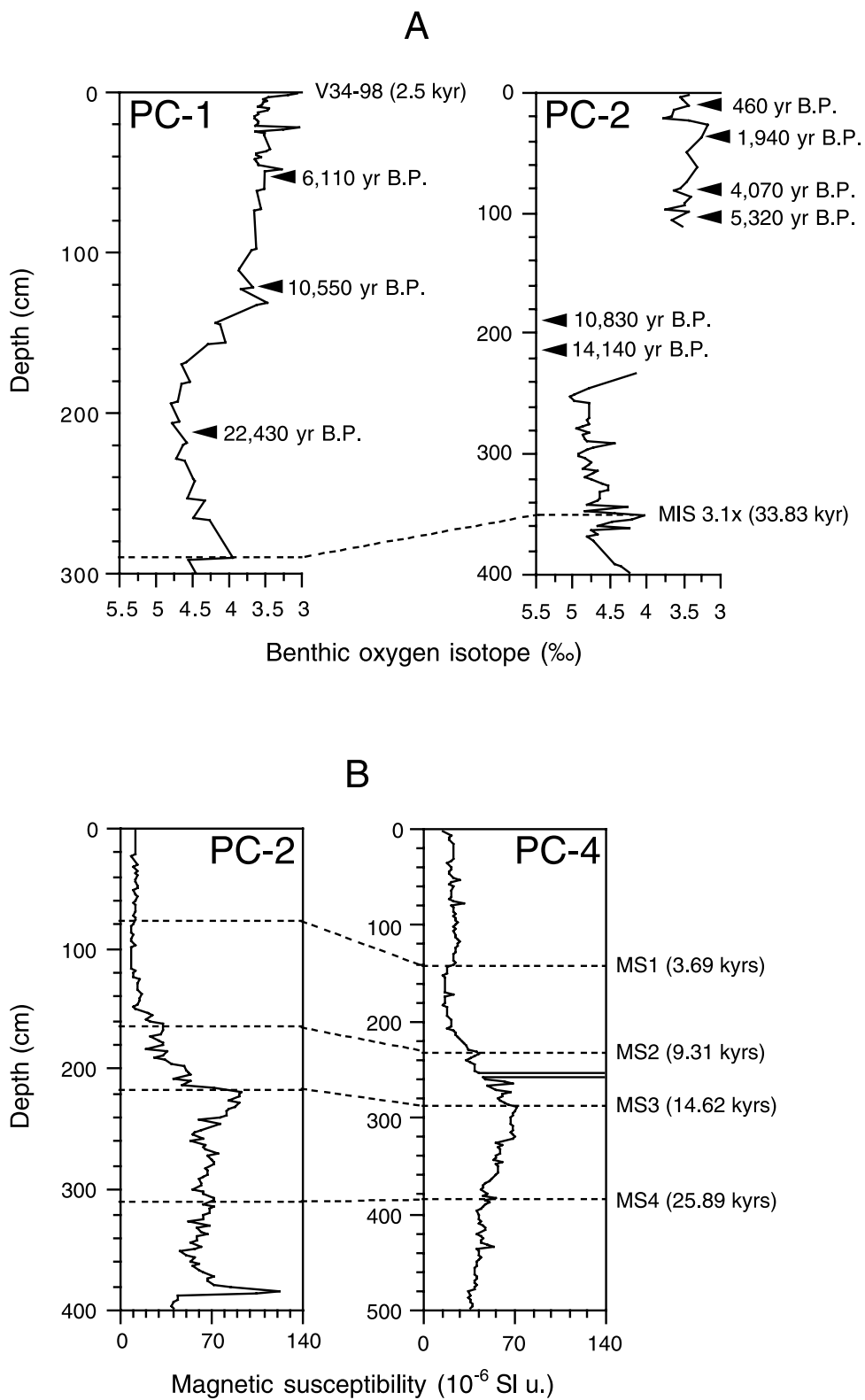
Figure 2. Down-core profiles of (a) benthic foraminiferal δ^{18}O in cores PC-1 and PC-2 and (b) magnetic susceptibility in PC-2 and PC-4. Triangles in Figure 2a represent AMS-^{14}C dating points.

Figure 3. Age-depth plots for Okhotsk Sea sediment cores (PC-1, PC-2, and PC-4).

increase coincident with the deglacial TOC peaks in PC-1 and PC-2. A third $CaCO_3$ peak is observed at about 5 ka, but only in PC-1. These postglacial peaks of carbonate have also been observed in sediment cores from the southeastern Okhotsk Sea and in the nearby Bering Sea [*Keigwin et al.*, 1992; *Gorbarenko*, 1996; *Gorbarenko et al.*, 2002a]. However, $CaCO_3$ contents in PC-4 were very low throughout the last 30 kyr with no postglacial peaks (Figure 6b).

[18] Biogenic opal in the Okhotsk Sea sediment is mostly derived from diatoms, which are the dominant phytoplankton group in the modern Okhotsk Sea. The biogenic opal contents in PC-1, PC-2, and PC-4 are relatively low (about 10%) in the last glacial and deglacial periods but became high (more than 40%) in sediments of the late Holocene (Figures 4d, 5d, and 6c). The low glacial and deglacial values persist until the early Holocene, whereas the TOC and $CaCO_3$ contents show an earlier increase within the deglacial period. The down-core profiles of opal content in the three cores are also similar to previous results in the southeastern Okhotsk Sea [*Keigwin et al.*, 1992; *Gorbarenko*, 1996; *Gorbarenko et al.*, 2002a].

4.4. Ice-Rafted Debris

[19] The volumes of IRD recorded in PC-2 and PC-4 are shown in Figures 5e and 6d. Here we defined IRD as terrigenous particles with diameters >63 μm on the basis of the study of sediment traps and surface sediments in the Okhotsk Sea [*Sakamoto et al.*, 2001]. High abundances of IRD should be the result of longer duration of sea ice cover, a larger volume of sea ice, or higher formation rates of sea ice in the colder climate regime. In general, the IRD records in PC-2 and PC-4 show high abundances in the glacial period and low abundances in the Holocene. Their variation patterns during the glacial-interglacial cycle coincide with

the sedimentary IRD record in the southern Okhotsk Sea (V34–90) [*Gorbarenko*, 1996]. The abundances of IRD in PC-2 are greater than PC-4 during the last glacial period. The decrease of IRD started in PC-2 at 15 ka, and IRD deposition disappeared completely in the Holocene. However, IRD contents in PC-4 gradually decreased from 10 to 5 ka but remained low in the late Holocene.

4.5. Lipid Biomarkers

[20] Terrestrial and marine biomarkers (C_{21}-C_{37} n-alkanes, C_{37}-C_{39} alkenones) were measured in the sediment cores. Molecular distributions of C_{25}-C_{35} n-alkanes are characterized by a strong odd to even carbon number predominance with a maximum at C_{29} or C_{31}. Their carbon preference indices (CPI) [*Bray and Evans*, 1961] vary between 3.7 and 5.4. The molecular distributions of n-alkanes are typical of terrestrial higher plant waxes [*Eglinton and Hamilton*, 1967]. In contrast, long-chain (C_{37}-C_{39}) alkenones are derived mostly from the coccolithophorids *E. huxleyi* and *G. oceanica*, Class Haptophyceae [*Conte et al.*, 1994]. Dinosterol (4a, 22, 23-trimethyl-5 α-cholest-22-en-3 β-ol) is thought to be derived from dinoflagellates [*Boon et al.*, 1979; *Robinson et al.*, 1984, 1987; *Volkman*, 1986]. These biomarkers are characteristic of certain microalgae and thus can be used as proxies for the reconstruction of past phytoplankton activity.

[21] Although brassicasterol (24-methylcholesta-5, 22E-dien-3 β-ol) is biosynthesized by most diatom species (over 90%) [*Volkman*, 1986], some haptophyceae algae also produce the brassicasterol that sometimes contributes 80% of the total sterols [*Volkman*, 1986; *Conte et al.*, 1994]. Even though diagenetic effects prevent quantitative assessment of biomarker source input, down-core profiles of their concentration and mass accumulation rates can be considered as a measure for reconstructing the variation of marine primary productivity and terrigenous input. Biomarkers have now been successfully applied in a number of paleoenvironmental studies in the late Quaternary [*Villanueva et al.*, 1997; *Ohkouchi et al.*, 1997; *Hinrichs et al.*, 1999; *Mangelsdorf et al.*, 2000; *Ikehara et al.*, 2000; *Sicre et al.*, 2000; *Zhao et al.*, 2000; *Ternois et al.*, 2000, 2001; *Sicre et al.*, 2001].

[22] The C_{37} alkenone contents in all cores were quite low (below 0.02 μg g^{-1}) during the glacial section (Figures 4e, 5f, and 6e). The peaks at MWP 1A and 1B are also recognized in C_{37} alkenones as well as in $CaCO_3$. However, C_{37} alkenone concentrations in PC-1 and PC-2 show a gradual decrease to the present after MWP 1B, while $CaCO_3$ contents in PC-2 show a sudden decrease at 11–10 ka. The third increase in $CaCO_3$ content during the mid-Holocene in PC-1 was also not recognized in the alkenone concentration. Although the contents of $CaCO_3$ were very low in PC-4 over the last 30 kyr, alkenones (0.2 ~ 1.0 μg g^{-1}) were abundantly detected throughout the last 15 kyr. Strong carbonate dissolution has recently been reported to occur in the water column of the modern Okhotsk Sea during sinking of carbonate particles. Hence carbonate probably was not preserved in the sediments of the Okhotsk Sea [*Broerse et al.*, 2000], and low $CaCO_3$ contents in sediment core (PC-4) during the last 15 kyr is likely due to dissolution in the water column and at the sediment surface.

PC-1
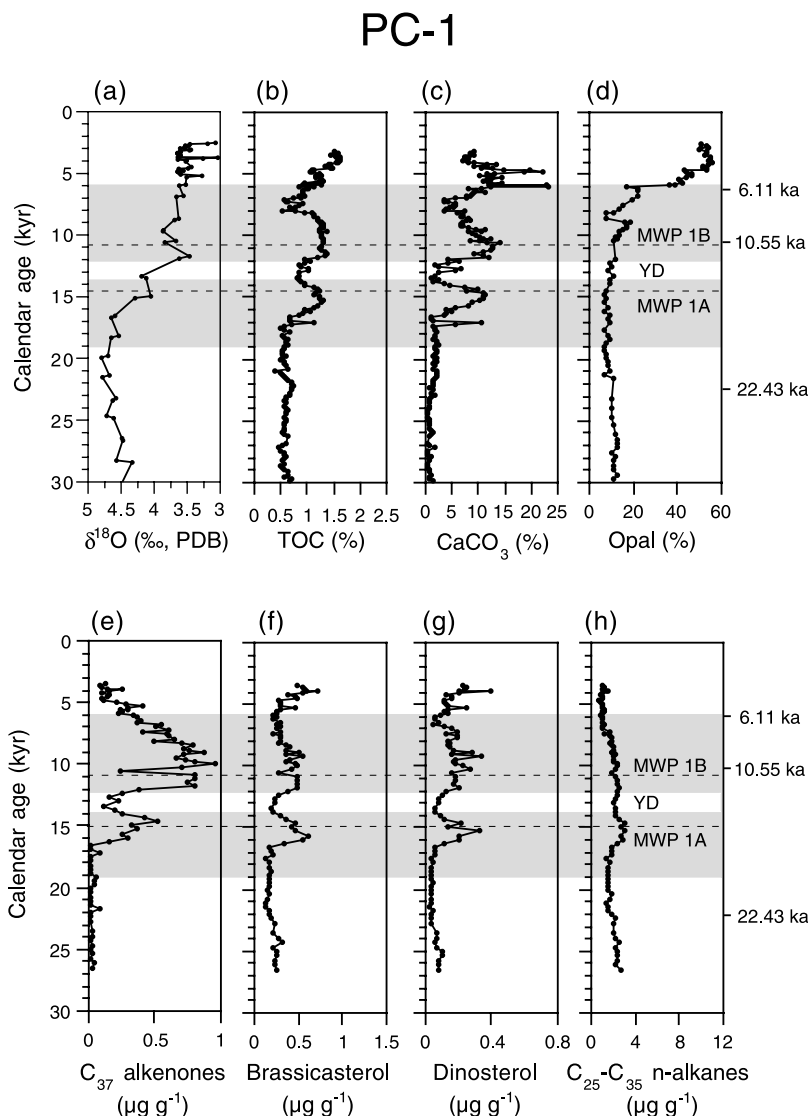
Figure 4. Down-core profiles of (a) benthic oxygen isotopes ($\delta^{18}O$), (b) total organic carbon (TOC), (c) biogenic opal, (d) $CaCO_3$, (e) C_{37} alkenones, (f) brassicasterol, (g) dinosterol, and (h) C_{25}-C_{35} n-alkanes in core PC-1. Shaded area represents the last deglacial period. The Younger Dryas event is marked by YD. Meltwater Pulse events 1A and 1B proposed by *Fairbanks* [1989] are represented by dotted lines. The dating points with their ages are denoted to the right of the figure.

In the modern Okhotsk Sea the dominant coccolithophores are *Coccolithus pelagicus* and *E. huxleyi* [*Broerse et al.*, 2000]. The sediment core profiles of coccoliths in PC-1 and PC-2 also show these two species as the dominant coccolith components over the last 15 kyr (H. Okada et al., personal communication, 2002). *E. huxleyi* is one of the major alkenone producers; hence we consider alkenones in the sediments to represent an input from *E. huxleyi* in spite of the fact that the coccolith plates ($CaCO_3$) are largely lost to dissolution. To better understand the change in the contribution of coccolithophorids to the primary production, the C_{37} alkenone concentrations were normalized to TOC (Figure 7). TOC-normalized C_{37} alkenones in all the cores were consistently high during the deglacial period. This supports the hypothesis that the contribution of coccolithophorids to primary production was enhanced during the deglaciation.

[23] Concentrations of brassicasterol, which is the dominant but not specific biomarker to diatoms [*Volkman*, 1986], show a variation similar to TOC content over the last 30 kyr (Figures 4f, 5g, and 6f). Brassicasterol concentrations in PC-1 and PC-2 began to increase at about 15-14 ka, peaked at around 10 ka, and stayed high in the Holocene. Core PC-4 also showed higher concentrations in the Holocene with two peaks before and after 3.5 ka. Opal contents increased rather uniformly after the deglacial period with a maximum during the last 3 kyr. The discrepancy between the brassicasterol and opal variations suggests the presence of an additional source of brassicasterol during these periods. The coincidence of the brassicasterol peaks in the deglacial with peaks of alkenone concentration suggests that haptophytes were a major contributor of the brassicasterol in the deglacial to early Holocene. Therefore we consider the down-core

PC-2
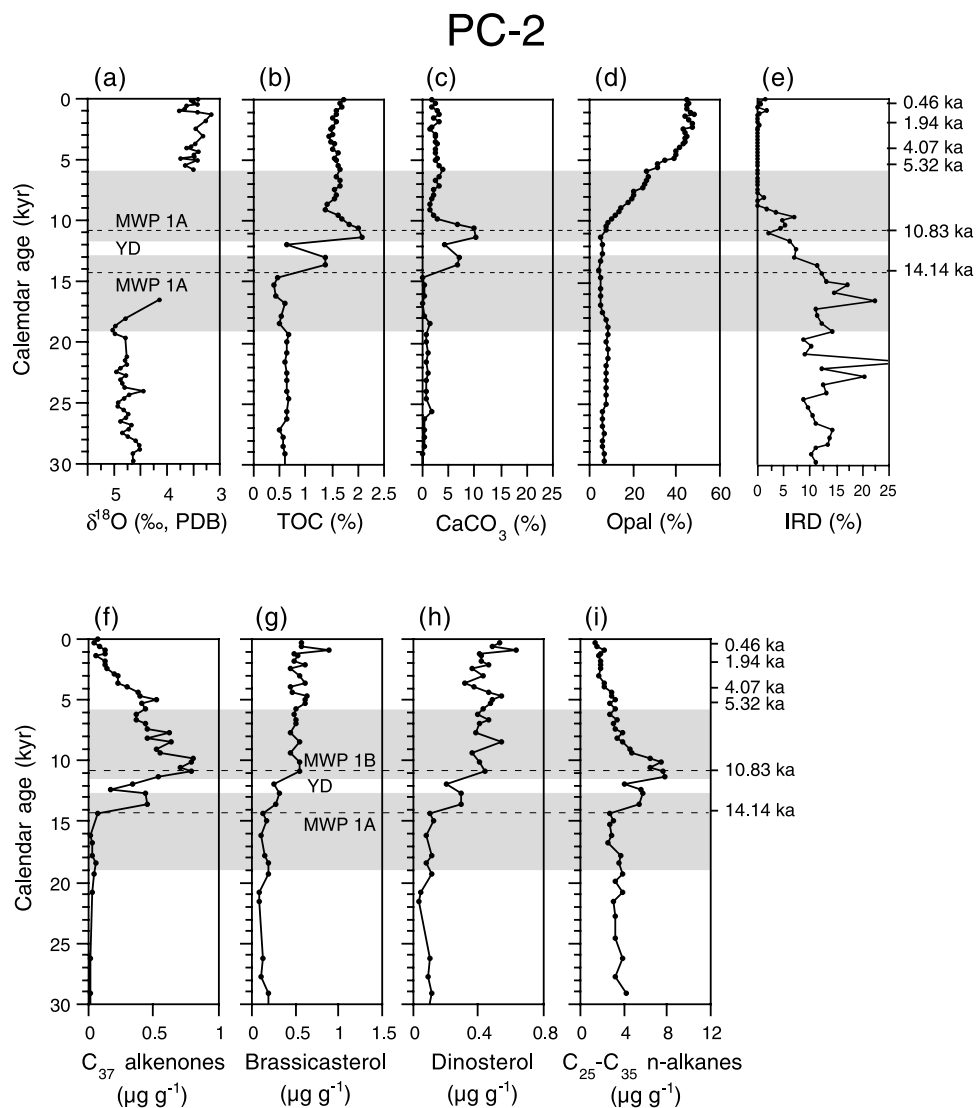
Figure 5. Down-core profiles of (a) benthic oxygen isotopes ($\delta^{18}O$), (b) total organic carbon (TOC), (c) biogenic opal, (d) $CaCO_3$, (e) ice-rafted debris (IRD), (f) C_{37} alkenones, (g) brassicasterol, (h) dinosterol, and (i) C_{25}-C_{35} n-alkanes in core PC-2.

profiles of biogenic opal to represent variations in diatom productivity better than brassicasterol.

[24] Although the concentrations of marine biomarkers in the sediments showed a drastic reduction during the glacial period (before 15 ka), TOC content did not decrease as much as the biomarkers. The $\delta^{13}C_{org}$ values in the sediments (from −22 to −21‰) indicate that sedimentary TOC during the glacial period is mostly derived from marine organisms [*Seki et al.*, 2003]. The reduction of marine biomarker contents in glacial sections may be related to their preferential remineralization rather than TOC.

[25] The alkenone unsaturation index ($U_{37}^{K'}$) has became a useful tool for estimating paleo sea surface temperature (SST) [*Brassell et al.*, 1986; *Prahl and Wakeham*, 1987]. However, the $U_{37}^{K'}$ in Okhotsk Sea sediments gave unexpectedly warm temperatures during the glacial that were almost the same as the Holocene level. Similar anomalies of alkenone SSTs during the glacial period have been recognized in sediments

of the Sea of Japan [*Ishiwatari et al.*, 2001], suggesting that higher $U_{37}^{K'}$ values in last glacial sections were a regional phenomenon of the semiclosed marginal seas in the northwestern Pacific rim. Warmer SST during the LGM can hardly be accepted because other paleoproxies have consistently suggested that a glacial climate regime in the sea was colder than at present [*Shiga and Koizumi*, 2000; *Gorbarenko et al.*, 2002a]. Rather, the sedimentary $U_{37}^{K'}$ records appear to have been modified by some environmental factors beside growth temperature. A detailed assessment of alkenone paleothermometry in Okhotsk Sea sediments is discussed in a separate paper [*Seki et al.*, 2004].

4.6. Mass Accumulation Rates (MAR) of TOC, CaCO₃, Opal, and Biomarkers

[26] It is commonly appreciated that MARs of biogenic component in sediments can be better used to reconstruct paleoproductivity than the concentrations because each

PC-4
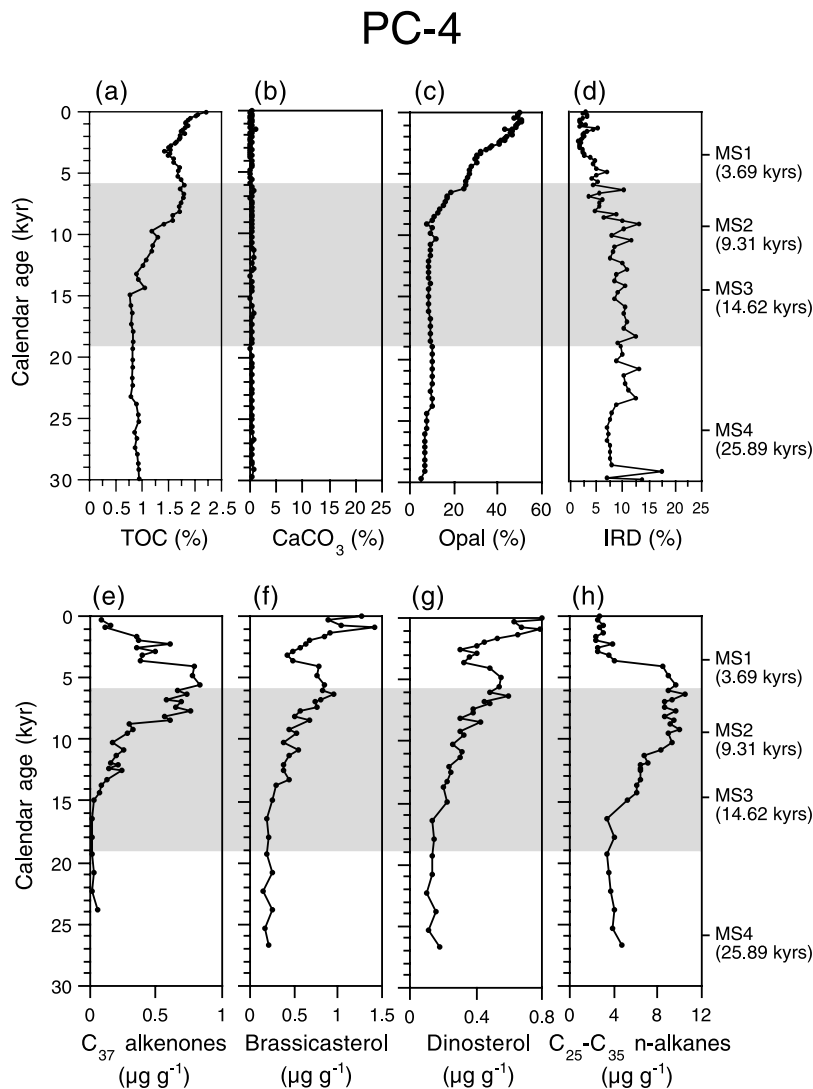
Figure 6. Down-core profiles of (a) total organic carbon (TOC), (b) biogenic opal, (c) $CaCO_3$, (d) ice-rafted debris (IRD), (e) C_{37} alkenones, (f) brassicasterol, (g) dinosterol, and (h) C_{25}-C_{35} n-alkanes in core PC-4.

component is diluted by other components. Hence we converted the concentrations of algal markers to MARs using the following equation:

$$MAR\left(g\ cm^{-2}\ kyr^{-1}\right) = DBD\left(g\ cm^{-3}\right) \times LSR\left(cm\ kyr^{-1}\right),\ (2)$$

where DBD and LSR are dry bulk density and linear sedimentation rate, respectively.

[27] Figure 8 shows MARs of the bulk sediments, TOC, biogenic opal, $CaCO_3$, C_{37} alkenones, and C_{25}-C_{35} n-alkanes in PC-1, PC-2, PC-4, and GGC-15 over the last 30 kyr. In general, the MARs of sediments in the XP cores are low in the glacial period and high after the deglaciation with an increase toward the core top. In contrast, the MAR of sediments in GGC-15 is characterized by the deglacial maximum. The variation patterns of TOC, biogenic opal, $CaCO_3$, and lipid biomarkers are essentially the same as the individual concentration profiles. Hence dilution effects are

not thought to be significant in the Okhotsk Sea sediments. *Gorbarenko et al.* [2002a] reported significant dissolution of carbonate in the sections of the late Holocene and Younger Dryas. High MARs of C_{37} alkenones during the deglaciation indicate high productivity of coccolithophorids during these periods. The concentration and MAR profiles of biomarkers strongly suggest that a phytoplankton succession from coccolithophores to diatoms occurred in the Okhotsk Sea during the last 15 kyr. Such a succession should be associated with changes in the oceanographic conditions, which in turn responded to global climate change.

5. Discussion

[28] To discuss the changes in the marine productivity of the late Quaternary Okhotsk Sea, we divided the last 0–30 ka into three periods on the basis of the productivity and phytoplankton succession. The first period was charac-
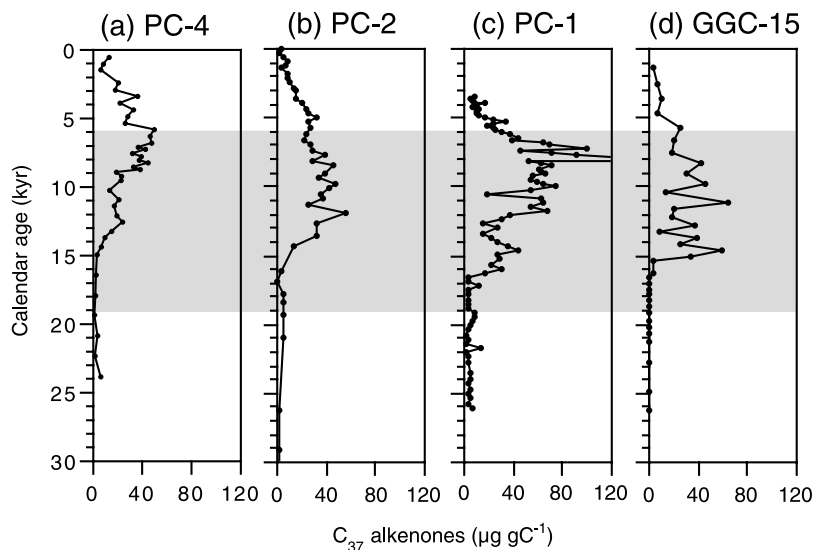
Figure 7. TOC-normalized concentrations of C_{37} alkenones in cores PC-1, PC-2, PC-4, and GGC-15 over the last 30 kyr.

terized by a less productive ocean (last 30-15 kyr). The second is the deglacial period (last 15-6 kyr), which was characterized by the high productivity of coccolithophorids. The third is the late Holocene (last 5-0 kyr), which has been characterized by high diatom productivity. Here we use these periods as defined above for the time intervals of discussion rather than marine isotope stages.

5.1. Decreased Primary Productivity in the Last Glacial Period

[29] All phytoplankton markers showed the lowest MARs in sediments of the last glacial period, suggesting the lowest productivity in the western and eastern regions of the Sea of Okhotsk during this period. The depressed productivity during the last glacial may have been caused by light limitation in the euphotic zone since sea ice strongly hampers light penetration into surface waters and thus depresses primary production. High abundances of IRD in cores PC-2 and PC-4 during the last glacial period suggest that sea ice was more widespread and extended further to the east than in the Holocene. Studies of diatom assemblages in sediment cores also suggest that perennial sea ice covered the western Okhotsk Sea in the last glacial period [*Shiga and Koizumi*, 2000; *Shiga et al.*, 2001]. These results together indicate that sea ice extended to the southeastern portion of the sea and covered the ocean for longer periods during the last glacial than at present. Thus sea ice extension during the last glacial should have decreased primary production, as suggested by previous study [*Ternois et al.*, 2001].

[30] Alternatively, a reduction in nutrient supply from the deep to the surface water could also have caused the low productivity. *Narita et al.* [2002] discussed evidence for the lowered productivity in the northwestern Pacific, including the Sea of Okhotsk, during the glacial period and attributed it to a decline in nutrient supply. Such a situation could be developed by the increased surface stratification that would

result from the melting of a large volume of sea ice in summer. Lowered productivity in the last glacial period has also been inferred for the Bering Sea, where seasonal sea ice is formed [*Nakatsuka et al.*, 1995]. The summer melting of a large volume of sea ice should produce large amounts of fresh water that promote a surface pycnocline. This should suppress vertical mixing between the surface and subsurface waters.

[31] Changes in the circulation of intermediate and deep waters can alter also the vertical distribution of nutrients. Enhanced ventilation of intermediate water should depress the supply of nutrients to the subsurface water because the intermediate water is more saline and contains less nutrients. Today's high productivity in the high-latitude North Pacific is attributed to the upwelling of NPDW, which contains high concentrations of nutrients. According to *Keigwin* [1998], the intermediate depths were better ventilated in the Sea of Okhotsk during the last glacial. It is generally accepted that global deep water circulation was reduced in the glacial age, weakening the upwelling of the NPDW in the North Pacific. These oceanographic changes together should have depressed the nutrient supply into the subsurface. As a result, the decreased supply of nutrients from the deeper to the surface water should have limited biological productivity in the Sea of Okhotsk during the last glacial period as well as in the northern region of the North Pacific [*Gorbarenko*, 1996; *Gorbarenko et al.*, 2002a; *Narita et al.*, 2002].

[32] The alkenone MARs were quite low in all the cores during the last glacial compared to other algal biomarkers. Preservation of alkenones in the sediments is thought to be generally better than those of other plankton-derived lipid biomarkers [*Sun and Wakeham*, 1994; *Gong and Hollander*, 1997, 1999]. Thus environmental conditions in the surface waters of the Okhotsk Sea are implicated in the suppressed growth of coccolithophords during the last glacial period, as discussed by *Ternois et al.* [2001]. In general, diatoms

PC-1

PC-2
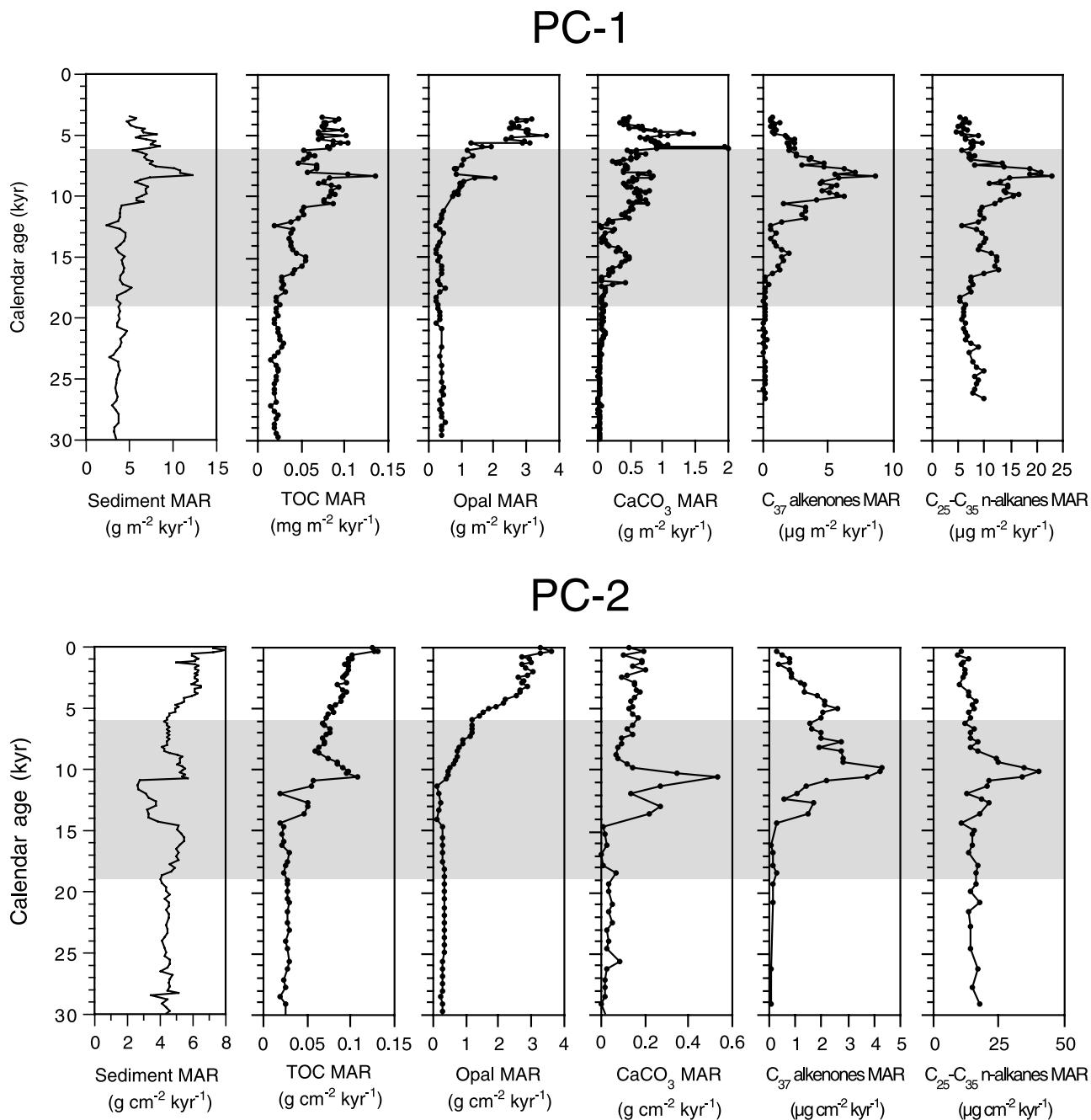
Figure 8. Calculated mass accumulation rates (MAR) of sediments, TOC, biogenic opal, $CaCO_3$, C_{37} alkenones, and C_{25}-C_{35} n-alkanes plotted against calendar age in cores PC-1, PC-2, PC-4, and GGC-15 over the last 30 kyr. The data for GGC-15 are from *Ternois et al.* [2001].
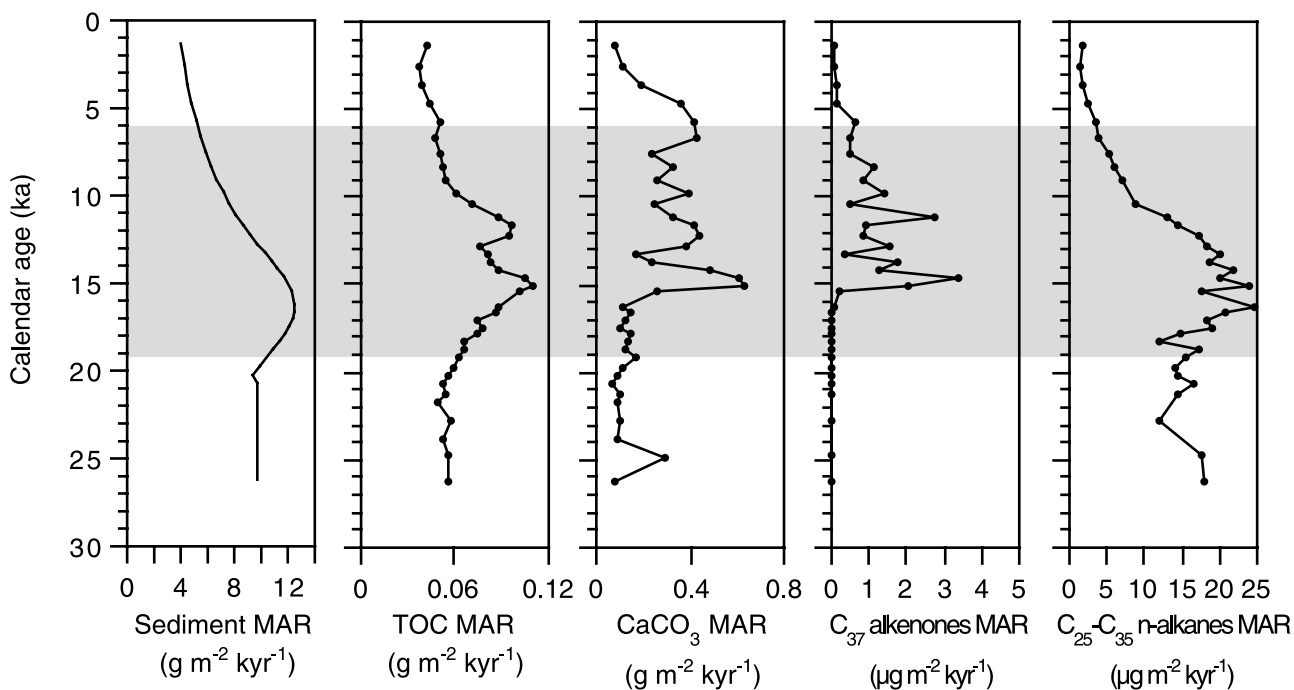
PC-4
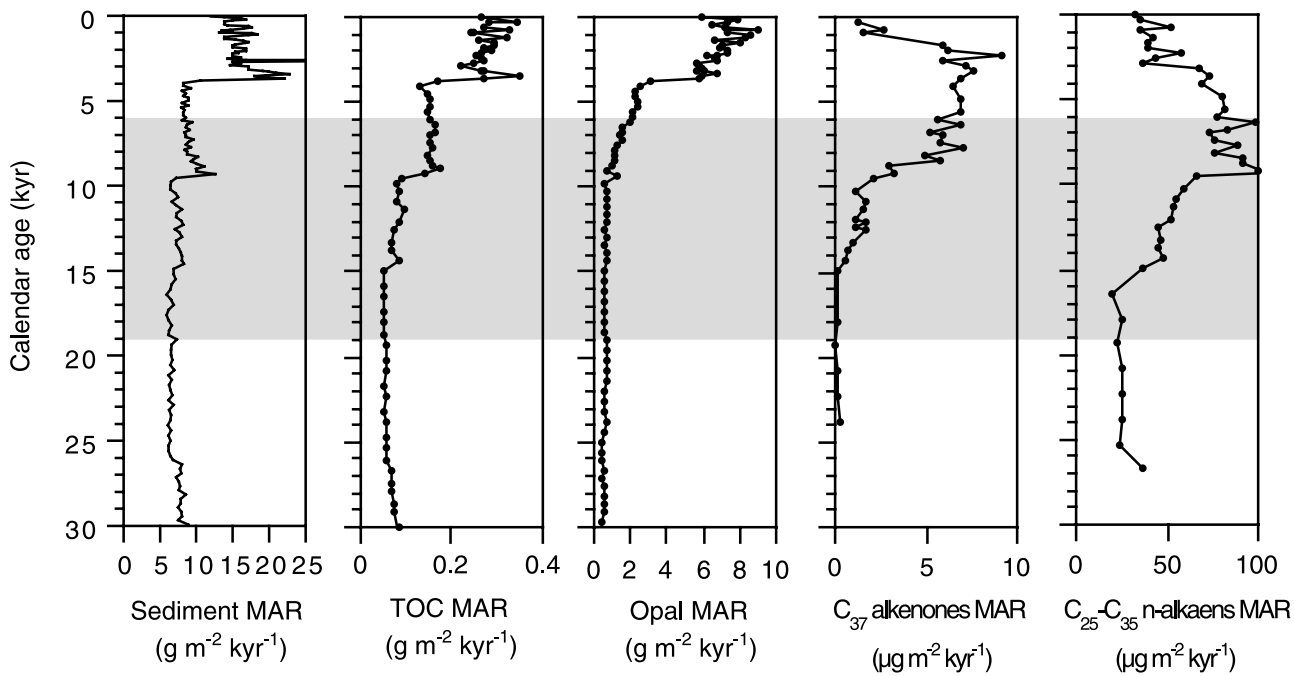
GGC-15

Figure 8. (continued)

preferentially utilize nitrate under the dissolved silicate-rich (>2 μM) conditions [*Egge and Aksenses*, 1992]. In fact, coccolithophorid blooms occur in the North Atlantic when silicate:nitrate ratios become low (<1). In the modern Okhotsk Sea, coccolithophores take over the primary producer role after diatoms consume all Si from the surface water in September [*Honda et al.*, 1997a, 1997b; *Honjo*, 1997; T. Nakatsuka et al., unpublished manuscript, 2003]. In the modern Sea of Okhotsk, coccolithophore production in the water column is primarily controlled by the availability of nutrients [*Broerse et al.*, 2000]. The increased dust flux during the glacial periods could have supplied silicate to the ocean's mixed layer, thus spurring the productivity of diatoms over coccoliths.

5.2. Enhanced Coccolithophorid Productivity During the Meltwater Pulse Events

[33] The timing of the deglacial increase in TOC contents and C_{37} alkenone concentrations in PC-1 (about 16 ka) seems to be about 2 kyr earlier than recorded in PC-2 (about 14 ka). The enhanced concentration and MAR of C_{37} alkenones in PC-4 during the last 15-10 kyr is much less evident than in the other cores. Hence enhanced productivity in the deglacial period may have begun on the eastern side of the sea and gradually spread westward. However, the AMS-^{14}C analyses in the Southern Okhotsk Sea sediments show that the initial $CaCO_3$ peak in the deglacial period can be well correlated with MWP event 1A, as well as the peak in PC-2 [*Gorbarenko et al.*, 2002a]. The apparent timing offsets between the results of PC-1 and PC-2 may therefore be due to limited chronology data for PC-1 rather than representing a real spatial difference.

[34] A weaker signal of alkenone MAR in PC-4 during the MWP events suggests that the deglacial coccolithophorid blooms were depressed in the northwest Okhotsk Sea (Figure 6). Comparison of the alkenone MARs with the IRD record from PC-2 and PC-4 indicates that the increases in alkenone MARs in PC-2 and PC-4 coincide with the timing of the IRD decrease. This suggests that the enhanced primary productivity in the deglacial period was associated with a retreat of sea ice. The southeastern sea should have disengaged the sea ice cover first in the early deglaciation, providing sufficient light for algal blooming. However, in the western and northern sea, the sea ice cover was prolonged and limited phytoplankton productivity until the late deglaciation. This scenario is supported by the sea ice history reconstructed from diatom floral analyses in Okhotsk Sea sediment cores [*Shiga and Koizumi*, 2000; *Shiga et al.*, 2001]. Although the age control for core PC-4 was achieved only by comparison of magnetic susceptibility with PC-2 (Ikehara et al., submitted manuscript, 2003), the observed trends and systematic consistency with sea ice history suggest that biological productivity responded to the retreat of sea ice in the deglaciation.

[35] The enhanced marine productivity during MWP events 1A and 1B was not a result of increased diatom activity, as indicated by the opal data. Thus oceanographic conditions during the deglaciation favored coccolithophorids suggesting that the supply of silicate to the surface was reduced during the deglacial period. Because silicate is supplied to the surface layer by strong winter convection, a weakened vertical mixing in winter and/or enhanced vertical stratification of the surface waters can depress the silicate supply. An abrupt negative shift of planktonic foraminiferal $\delta^{18}O$ during MWP 1A has been recognized in the Southern Okhotsk Sea and nearby Bering Sea, suggesting massive discharge of fresh water into the seas in the northwestern region of the subarctic northwest Pacific and subsequent replenishment of less saline waters to the surface [*Gorbarenko*, 1996; *Gorbarenko et al.*, 2002a]. This should have promoted development of well-stratified surface waters, providing better light conditions for the coccolithophorids.

[36] Because a continental ice sheet did not develop in eastern Siberia [*Velichko et al.*, 1997a], the source of meltwater discharged into the Sea of Okhotsk must have originated from other regions. *Gorbarenko* [1996] discussed Kamchatka icebergs as one of the possible sources. Input of fresh water from the Amur River is also possible for promoting stratification. According to pollen data from eastern Siberia, precipitation increased from the last glacial to the deglacial period [*Velichko et al.*, 1997b; *Edwards et al.*, 2001]. Consequently, the silicate supply from deep to surface water might have been suppressed, allowing the bloom of coccolithophorids during the MWP events.

5.3. Nutrient Input From the Continental Shelf in the Deglacial Period?

[37] Terrestrial inputs of micro (e.g., iron) and macro (nitrate, ammonia, phosphate, and silicate) nutrients are important factors in controlling the biological productivity of marginal seas. Hence enhanced terrestrial input of nutrients in the past could be the cause of increases in biological productivity. Interestingly, the MARs of alkenones (Figure 7) and C_{25}-C_{35} *n*-alkanes in all the cores covaried during the last 15 kyr. Good correlations (r > 0.8) between the C_{25}-C_{35} *n*-alkane and alkenone MARs in PC-1, PC-2, and PC-4 over the last 15 kyr imply a linkage between enhanced haptophyte productivity and increased terrigenous input in the past Okhotsk Sea as discussed by *Ternois et al.* [2001].

[38] Sea level was lower in the last glacial period owing to the development of continental ice sheets [*Fairbanks*, 1989]. Estimated sea level during the LGM was −135 to −140 m in the Bonaparte Gulf, Australia [*Yokoyama et al.*, 2000]. According to *Seki et al.* [2003], the increase in MARs of terrestrial biomarkers found in Okhotsk Sea cores during the deglaciation can be interpreted to be linked to a submergence of the shelf owing to the rise of sea level. The enhanced inputs of terrestrial organic matter during deglaciation were probably initiated by resuspension of materials over the submerged land shelf in the northwestern sea through tidal current and subsequently transported to the central Sea of Okhotsk by the East Sakhalin Current as well as in intermediate water [*Seki et al.*, 2003].

[39] The depth of tidal mixing with high turbidity on the northwestern continental shelf is more than 50 m in the modern Okhotsk Sea [*Nakatsuka et al.*, 2002]. The water depth of the northwestern continental shelf must have been shallower during the deglacial period. Under such oceanographic conditions, resuspended particles, as well as

micronutrients and macronutrients, over the newly flooded continental shelf may have been transported from the northwest to the south by the East Sakhalin Current. Hence nutrients transported in this way may have been utilized by phytoplankton to produce the increase in biological productivity recorded in the central Okhotsk Sea.

[40] *Ternois et al.* [2001] proposed that an increased terrestrial input of nutrients enhanced the productivity of the sea during the deglacial period. Because land soils generally contain silicate, they are an important source of this nutrient for diatom production. It is reported that silicate is the most abundant nutrient in Russian rivers with an average concentration of 23.2 μM [*Lara et al.*, 1998; *Lobbes et al.*, 2000]. The mean concentration of silicate is one order of magnitude higher than that of dissolved inorganic nitrogen (nitrate, nitrite, and ammonium) [*Lobbes et al.*, 2000]. Although there are no silicate data for the Amur River, it can be expected that waters in the Amur River are rich in silicate as they are in other Russian rivers.

[41] Culture and field experiments have shown that *E. huxleyi* is a good phosphate competitor [*Riegman et al.*, 1992; *Egge and Heimdal*, 1994; *Riegman et al.*, 2000], and thus an increase in phosphate level may be a potential cause for promoting *E. huxleyi* productivity. However, increases in the concentration of phosphate from terrestrial input seem unlikely because the phosphate (N/P) ratio in seawater near the estuary of the Amur River is significantly lower than that in offshore surface waters in the Sea of Okhotsk (T. Nakatsuka, unpublished manuscript, 2003), suggesting a low concentration of phosphate in the river waters. Hence the terrestrial input of nutrients cannot by itself act to promote coccolithophorid productivity. As a result, the increased stratification of surface waters with the deglacial global warming is considered the likely cause for deglacial coccolithophorid blooms rather than diatom blooms.

5.4. Succession From Coccolithophorids to Diatoms in the Mid-Holocene

[42] Since the mid-Holocene, haptophyte productivity has gradually decreased to present levels. Terrestrial inputs from the continental shelf also likely decreased owing to the end of transgression and a decrease in fluvial input from the Amur River [*Seki et al.*, 2003]. In contrast, diatoms gradually increased their productivity and eventually became the dominant primary producer in this sea. The succession of dominant phytoplankton suggests that oceanographic conditions in the Okhotsk Sea changed significantly since the mid-Holocene. One possible explanation is a breakdown of surface water stratification, with increasing silicate supply from subsurface waters in the late Holocene. A pollen study in east Eurasia suggests that precipitation was greater in the mid-Holocene than at present (increased by 154 mm) [*Monserud et al.*, 1998]. A decrease in precipitation in the late Holocene may in part have contributed to an increase in the salinity of surface waters, thus inducing a breakdown of surface stratification and the renewal of silicate supply from the subsurface water.

[43] Another potential cause of the phytoplankton succession is a change in the silicate concentration of the deeper source water. *Narita et al.* [2002] explained the enhanced

diatom productivity in the Okhotsk Sea during the late Holocene in this manner. Enhanced marine productivity at the Emperor Seamount region of the northwestern Pacific in the interglacial period has been explained by the intensified upwelling of NPDW [*Narita et al.*, 2002]. Because of the well-developed surface layer that would have resulted from meltwater discharge during the deglacial period, upwelling of nutrient-rich deep water might have intensified after deglaciation in the Sea of Okhotsk.

## 5.5. Biological and Hydrological Effects of CO_2 Exchange Between the Ocean and Atmosphere

[44] Concentrations of atmospheric CO_2 changed from around 200 ppm in the last glacial maximum to 280 ppm in the Holocene [*Petit et al.*, 1999]. The population of land biota was reduced in the glacial period [*Shackleton*, 1977; *Crowley*, 1995], suggesting a greater oceanic storage of carbon than today and during the deglacial period. A number of mechanisms related to oceanic biological activity have been proposed to explain the changes in atmospheric CO_2 concentration. In the way of biological effects, (1) changes in the intensity of the biological pump [*Sarmiento and Toggweiler*, 1984] and (2) changes in opal/carbonate fluxes [*Dymond and Lyle*, 1985] have been proposed to explain the glacial-interglacial atmospheric CO_2 change.

[45] In the latter hypothesis the succession between diatom and coccolithophorid floras play an important role in the global carbon cycle. Although the biological activity of both groups is involved with CO_2 gas exchange between the ocean and the atmosphere, the roles they play are opposite. Whereas diatom blooms act efficiently as a sink for atmospheric CO_2 [*Berger et al.*, 1989], coccolithophorid blooms have been suggested to be a potential source of atmospheric CO_2 because the calcification process (i.e., $CaCO_3$ formation from Ca^{2+} and $2HCO_3^-$) decreases alkalinity twice as much as dissolved inorganic carbon. Calcification hence produces more protons in the seawater, releasing more oceanic CO_2 to the atmosphere. Because calcification by coccolithophorids is loosely coupled to photosynthesis, pCO_2 is increased at higher calcification:photosynthesis production ratios.

[46] In terms of surface hydrology, *Siegenthaler and Wenk* [1984] proposed that changes in vertical mixing in the high-latitude oceans significantly altered the pCO_2 in surface waters. Stratification of the surface reduces pCO_2, whereas enhanced vertical mixing increases surface pCO_2.

[47] Although this and previous studies [*Keigwin et al.*, 1992; *Gorbarenko*, 1996; *Gorbarenko et al.*, 2002a] consistently show that diatom productivity during the glacial period was depressed in the subarctic regions compared to interglacials, the stratification of surface water in summer and enhanced sea ice cover during the glacial winter reduced CO_2 release from the ocean to atmosphere [*Narita et al.*, 2002]. Moreover, a drastic reduction of coccolithophore productivity during the last glacial period would have contributed to a significantly reduced CO_2 release to the atmosphere in the subarctic Pacific region.

[48] In contrast, the abrupt enhancement of coccolithophorid productivity during MWP events might have pro-
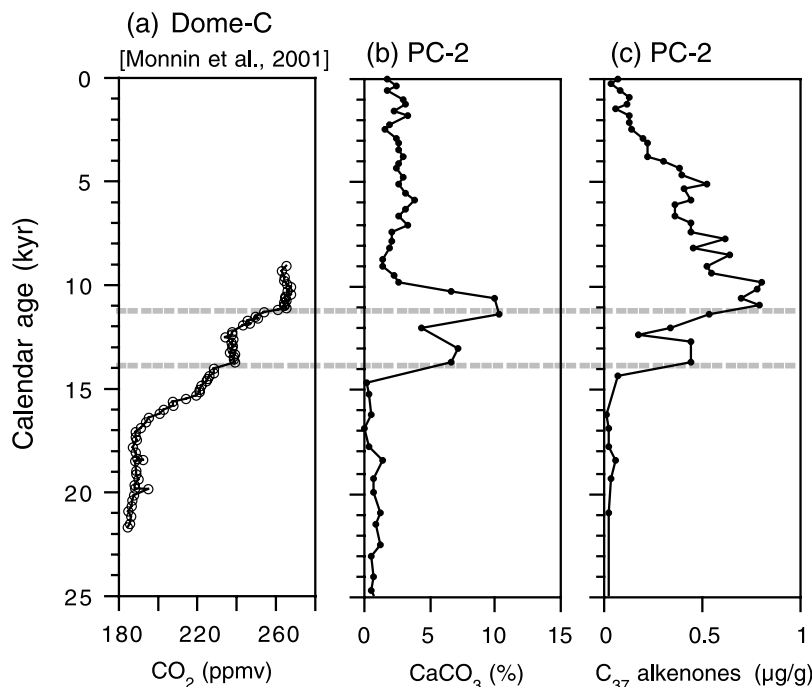
Figure 9. Comparison of $CaCO_3$ and C_{37} alkenones records in the Okhotsk Sea sediment core (PC-2) with the CO_2 record in the Dome-Concordia Antarctic ice core [*Monnin et al.*, 2001].

moted a release of oceanic CO_2 to the atmosphere. Studies of Antarctic ice cores suggest that the Southern Ocean played an important role in regulating atmospheric CO_2 concentrations during the glacial-interglacial cycles [*Petit et al.*, 1999]. Our study suggests that enhanced coccolitho-phorid activity in the northwestern North Pacific contributed to a potential release of oceanic CO_2 to the atmosphere in the MWP events. This hypothesis is consistent with high-resolution study of the Dome Concordia ice core, which suggests that processes in both the tropics and the Northern Hemisphere had substantial effects on the increase in atmospheric CO_2 at 14 and 11 ka [*Monnin et al.*, 2001]. A comparison of alkenone and $CaCO_3$ concentrations in PC-2 with CO_2 concentrations in the Dome C ice core [*Monnin et al.*, 2001] indicates that the timing of abrupt increases in alkenone concentrations coincide well with the ice core CO_2 at 14 and 11 ka (see Figure 9). Deglacial $CaCO_3$ peaks have also been reported in sediment cores taken from the northwest Pacific and the Bering Sea [*Keigwin et al.*, 1992; *Gorbarenko*, 1996], suggesting an enhanced productivity of coccoliths and/or foraminifera during MWP events in the high-latitude North Pacific. The deglacial enhancement of coccolithophore productivity in the northwest subarctic North Pacific may have links with the global-scale increase in the atmospheric CO_2 at 14 and 11 ka. However, if the deglacial coccolith blooms were instead caused by the stratification of surface waters that developed during MWP events, the biological effect on pCO_2 increase would be modified because increased surface stratification could act as an inhibitor of oceanic CO_2 release. Hence a quantification of net CO_2 exchange from both biological and hydrological effects is needed to further
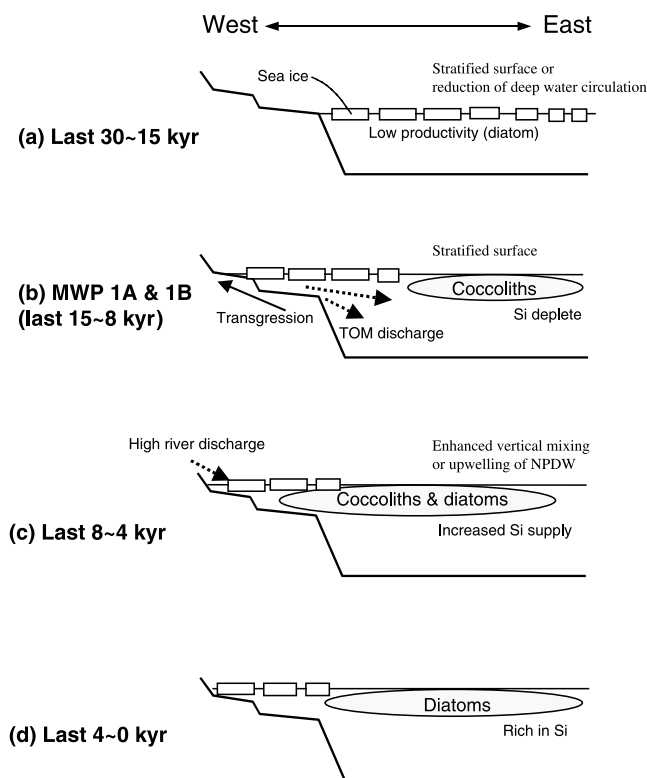
Figure 10. Reconstructed changes in the productivity and hydrography of the Sea of Okhotsk from the last glacial period to the present.

elucidate the impact of deglacial coccolithophorid blooms on the CO_2 system in the northwestern North Pacific.

6. Summary and Conclusions

[49] Changes in the dominant phytoplankton species and surface hydrography as estimated from alkenone and biogenic opal records over the last 30 kyr are summarized in Figure 10. Between 30 and 15 ka the Okhotsk Sea was covered with sea ice (Figure 10a). Phytoplankton productivity in the sea was low owing to light limitation and/or lowered nutrient supply, with coccolithophorid productivity being drastically depressed. During MWP events 1A and 1B, coccolithophorid blooms occurred in the southern sea, responding to a retreat of sea ice and increased meltwater discharge (Figure 10b). In contrast, diatom productivity was low owing to a deficiency in silicate supply during the deglacial period. The input of terrestrial organic matter was enhanced as a result of rising sea level. In the early and mid-Holocene, coccolithophorid blooms spread out toward the western part of the sea, following a retreat of sea ice in this region (Figure 10c). Replenishment of the surface with fresh water from the Amur River resulted in stratification in the surface mixed layer and suppressed the supply of silicate from subsurface waters. In the late Holocene, diatoms became the dominant species as a result of an increased supply of silicate from the subsurface to euphotic zone that was probably caused by enhanced vertical mixing between the surface and subsurface waters in winter (Figure 10d) and/or by an increased supply of silicate to the subsurface water from the North Pacific. With increased nutrient supply, coccolithophorids could not compete with diatoms and the biomass of coccolithophorids was reduced.

[50] The MARs of alkenones and biogenic opal also show the drastic change in phytoplankton composition from coccolithophorids in the deglacial to diatoms in the late Holocene with lower overall productivity during the glacial period. This phytoplankton succession should be responsive to the change of silicate supply to the surface layer. Comparisons among the three sediment cores indicate that enhanced coccolithophorid productivity in the deglacial began in the eastern region of the Sea of Okhotsk and subsequently extended to the western region. This spatial and temporal distribution of productivity is consistent with the sea ice history reconstructed by IRD, suggesting that the presence of sea ice is the key factor that controls biological productivity in the sea over a glacial-interglacial cycle. In light of potential biological effects on CO_2 exchange between the ocean and atmosphere, the Sea of Okhotsk may have acted as a source of atmospheric CO_2 during MWP events 1A and 1B, in contrast to the modern Okhotsk Sea which acts as a sink for atmospheric CO_2.

References

Alfultis, M. A., and S. Martin (1987), Satellite passive microwave studies of Sea of Okhotsk ice cover and relation to oceanic processes, 1987–1982, *J. Geophys. Res.*, 92, 13,013–13,028.

Archer, D. (1991), Modeling the calcite lysocline, *J. Geophys. Res.*, 96, 17,037–17,050.

Berger, W. H., V. S. Wefer, G. Smetacek (1989), Ocean productivity and paleoproductivity-An overview, in *Productivity of the Ocean: Present and Past*, edited by W. H. Berger, V. S. Smetacek, and G. Washington, John Wiley, Hoboken, N. J.

Boon, J. J., W. I. C. Eijpstra, F. de Lange, J. W. deLeeuw, M. Yoshioka, and Y. Shimizu (1979), Black Sea sterol—A molecular fossil for dinoflagellate blooms, *Nature*, 277, 125–127.

Brassell, S. C., G. Eglinton, I. T. Marlowe, U. Pflaumann, and M. Sarnthein (1986), Molecular stratigraphy: A new tool for climatic assessment, *Nature*, 320, 129–133.

Bray, E. E., and E. D. Evans (1961), Distributions of n-paraffins as a clue to recognition of source beds, *Geochim. Cosmochim. Acta*, 22, 2–15.

Broecker, W. S., M. Klas, E. Clark, G. Bonani, S. Ivy, and W. Wolfli (1991), The influence of $CaCO_3$ dissolution on core top radiocarbon ages for deep-sea sediments, *Paleoceanography*, 6, 593–608.

Broerse, A. T. C., P. Zieveri, and S. Honjo (2000), Coccolithophore (-$CaCO_3$) flux in the Sea of Okhotsk: Seasonality, settling and alteration processes, *Mar. Micropaleontol.*, 39, 179–200.

Conte, M. H., J. K. Volkman, and G. Engliton (1994), Lipid biomarkers of the Haptophyta, in *The Haptophyte Algae*, edited by J. C. Green et al., pp. 351–377, Clarendon Univ. Press, Oxford.

Crowley, T. J. (1995), Ice age terrestrial carbon changes revisited, *Global Biogeochem. Cycles*, 9, 377–389.

Dymond, J., and M. Lyle (1985), Flux comparisons between sediments and sediment traps in the eastern Tropical Pacific: Implications for atmospheric CO_2 variations during the Pleistocene, *Limnol. Oceanogr.*, 39, 699–712.

Eadie, B. J., and L. M. Jeffrey (1973), $\delta^{13}C$ analysis of oceanic particulate organic matter, *Mar. Chem.*, 1, 199–209.

Edwards, M. E., C. J. Mock, B. P. Finney, V. A. Barber, and P. J. Bartlein (2001), Potential analogues for paleoclimatic variations in eastern interior Alaska during the past 14,000 yr: Atmospheric-circulation controls of regional temperature and moisture responses, *Quat. Sci. Rev.*, 20, 189–202.

Egge, J. K., and D. L. Aksenes (1992), Slicate as regulating nutrient in phytoplankton competition, *Mar. Ecol. Prog. Ser.*, 83, 281–289.

Egge, J. K., and B. R. Heimdal (1994), Blooms of phytoplankton including Emiliania huxleyi (Haptophyta): Effects of nutrient supply in different N:P ratios, *Sarsia*, 79, 333–348.

Eglinton, G., and R. J. Hamilton (1967), Leaf epicuticular waxes, *Science*, 156, 1322–1335.

Emerson, S., and M. Bender (1981), Carbon fluxes at the sediment-water interface of the deep-sea: Calcium carbonate preservation, *J. Mar. Res.*, 39, 139–162.

Fairbanks, R. G. (1989), A 17,000-year glacio-eustatic sea level record: Influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation, *Nature*, 342, 637–642.

Freeland, H. J., A. S. Bychkov, F. Whitney, C. Taylor, C. S. Wong, and G. I. Yurasov (1998), WOCE section PIW in the Sea of Okhotsk, 1. Oceanographic data description, *J. Geophys. Res.*, 103, 15,613–15,623.

Gladyshev, S., S. Martin, S. Riser, and A. Figurkin (2000), Dense water production on the northern Okhotsk shelves: Comparison of ship-based spring-summer observations for 1996 and 1997 with satellite observations, *J. Geophys. Res.*, 105, 26,281–26,299.

Gong, C., and D. J. Hollander (1997), Differential contribution of bacteria to sedimentary organic matter in oxic and anoxic environments, Santa Monica Basin, California, *Org. Geochem.*, 26, 545–563.

Gong, C., and D. J. Hollander (1999), Evidence for the differential degradation of alkenones under contrasting bottom water oxygen conditions: Implication for paleotemperature reconstruction, *Geochem. Cosmochim. Acta*, 63, 405–411.

Gorbarenko, S. A. (1996), Stable isotope and lithologic evidence of late-glacial and Holocene oceanography of Northwestern Pacific and its marginal seas, *Quat. Res.*, 46, 230–250.

Gorbarenko, S. A., T. A. Khusid, I. A. Basov, T. Oba, J. R. Southon, and I. Koizumi (2002a), Glacial-Holocene environment of the southeastern Okhotsk Sea: Evidence from geochem-

ical and paleontological data, *Palaeoceanogr. Palaeoclimatol. Palaeoecol.*, *177*, 237–263.

Gorbarenko, S. A., D. Nürnberg, A. N. Derkachev, A. S. Astakhov, J. R. Southon, and A. Kaiser (2002b), Magnetostratigraphy and tephrochronology of the Upper Quaternary sediments in the Okhotsk Sea: Implication of terrigenous, volcanogenic and biogenic matter supply, *Mar. Geol.*, *183*, 107–129.

Hinrichs, K.-U., R. R. Schneider, P. J. Muller, and J. Rullküter (1999), A biomarker perspective on paleoproductivity variations in two Late Quaternary sediment sections from the southeast Atlantic Ocean, *Org. Geochem.*, *30*, 341–366.

Honda, C. M., M. Kusakabe, and S. Nalabayashi (1997a), The efficiency of biological pump in the western North Pacific, in *Biogeochemical Processes in the North Pacific*, edited by S. Tsunogai, pp. 224–232, Jpn. Mar. Sci. Found., Tokyo.

Honda, C. M., M. Kusakabe, S. Nakabayashi, S. J. Manganini, and S. Honjo (1997b), Change in pCO$_2$ through biological activity in the marginal seas of the western North Pacific: The efficiency of the biological pump estimated by a sediment trap experiment, *J. Oceanogr.*, *53*, 645–662.

Honda, M. C., K. Imai, Y. Nojiri, F. Hoshi, T. Sugawara, and M. Kusakabe (2002), The biological pump in the northwestern North Pacific based on fluxes and major components of particulate matter observed by sediment-trap experiments (1997–2000), *Deep Sea Res. Part II*, *49*, 5595–5625.

Honjo, S. (1996), Fluxes of particles to the interior of the open oceans, in *Particle Fluxes in the Ocean*, edited by V. Ittekkot et al., pp. 91–154, John Wiley, Hoboken, N. J.

Honjo, S. (1997), The northwestern Pacific Ocean, a crucial ocean region to understand global change: Rationale for new international collaborative investigations, in *Biogeochemical Processes in the North Pacific*, edited by S. Tsunogai, pp. 1–15, Jpn. Mar. Sci. Found., Tokyo.

Ikehara, M., K. Kawamura, N. Ohkouchi, M. Murayama, T. Nakatsuka, and A. Taira (2000), Variation of terrestrial input and marine productivity in the Southern Ocean (48°S) during the last two deglaciations, *Paleoceanography*, *15*, 170–180.

Ishiwatari, R., M. Houtatsu, and H. Okada (2001), Alkenone-sea surface temperatures in the Japan Sea over the past 36 kyrs: Warm temperatures at the last glacial maximum, *Org. Geochem.*, *32*, 57–67.

Kawamura, K. (1995), Land-derived lipid class compounds in the deep-sea sediments and marine aerosols from North Pacific, in *Biochemical Processes and Ocean Flux in the Western Pacific*, edited by H. Sakai and Y. Nozaki, pp. 31–51, Terra Sci., Tokyo.

Keigwin, L. D. (1998), Glacial-age hydrography of the far northwest Pacific Ocean, *Paleoceanography*, *13*, 323–339.

Keigwin, L. D., G. A. Joans, and P. N. Froelich (1992), A 15,000 year paleoenvironmental record from Meiji Seamount, far northwestern Pacific, *Earth Planet. Sci. Lett.*, *111*, 425–440.

Lara, R. J., V. Rachold, G. Kattner, H. W. Hubberten, G. Guggenberger, A. Skoog, and D. N. Thomas (1998), Dissolved organic matter and nutrients in the Lena River, Siberian Arctic: Characteristics and distribution, *Mar. Chem.*, *59*, 301–309.

Lobbes, J. M., H. P. Fitznar, and G. Kattner (2000), Biochemical characteristics of dissolved and particulate organic matter in Russian rivers entering the Arctic Ocean, *Geochim. Cosmochim. Acta*, *64*, 2973–2983.

Macnaughton, S. J., T. L. Jenkins, M. H. Wimpee, M. R. Cormiér, and D. C. White (1997), Rapid extraction of lipid biomarkers from pure culture and environmental samples using pressurized accelerated hot solvent extraction, *J. Microbiol. Methods*, *31*, 19–27.

Mangelsdorf, K., U. Güntner, and J. Rullkötter (2000), Climatic and oceanographic variations on the California continental margin during the last 160 kyr, *Org. Geochem.*, *31*, 829–846.

Marlowe, I. T., J. C. Green, A. C. Neal, S. C. Brassell, G. Eglinton, and P. A. Course (1984), Long chain (C_{37}–C_{39}) alkenones in the Prymnesiophyceae: Distribution of alkenones and other lipids and their taxonomic significance, *Br. Phycol.*, *19*, 203–216.

Martin, S., R. Drucker, and R. Yamashita (1998), The production of ice and dense shelf water in the Okhotsk Sea polynyas, *J. Geophys. Res.*, *103*, 27,771–27,782.

Martinson, D. G., N. G. Pisias, J. D. Hays, J. Imbrie, T. C. Moore, and N. J. Shackleton (1987), Age dating and the orbital theory of the ice ages: Development of a high resolution 0 to 300,000-year chronostratigraphy, *Quat. Res.*, *27*, 1–29.

Meyers, P. A. (1994), Preservation of elemental and isotopic source identification of sedimentary organic matter, *Chem. Geol.*, *144*, 289–302.

Monnin, E., A. Indermühle, A. Dällenbach, J. Flückiger, B. Stauffer, T. F. Stocker, D. Raynaud, and J.-M. Barnola (2001), Atmospheric CO$_2$ concentrations over the last glacial termination, *Science*, *291*, 112–115.

Monserud, R. A., N. M. Tehebakova, and O. V. Denissenko (1998), Reconstruction of the mid-Holocene paleoclimate of Siberia using a bioclimatic vegetation model, *Palaeoceanogr. Palaeoclimatol. Palaeoecol.*, *139*, 15–36.

Mortlock, R. A., and P. N. Froelich (1989), A simple method for the rapid determination of biogenic opal in pelagic sediments, *Deep Sea Res.*, *36*, 1415–1426.

Mortlock, R. A., C. D. Charles, P. N. Froelich, M. A. Zibella, J. Saltzman, J. D. Hays, and L. H. Burkle (1991), Evidence of lower productivity in the Antarctic Ocean during the last glaciation, *Nature*, *351*, 220–223.

Nakatsuka, T., K. Watanabe, N. Handa, and E. Matsumoto (1995), Glacial to interglacial surface nutrient variations of Bering deep basins recorded by δ^{13}C and δ^{15}N of sedimentary organic matter, *Paleoceanography*, *10*, 1047–1061.

Nakatsuka, T., C. Yoshikawa, M. Toda, K. Kawamura, and M. Wakatsuchi (2002), An extremely turbid intermediate water in the Sea of Okhotsk: Implication for the transport of particulate organic matter in a seasonally ice-bound sea, *Geophys. Res. Lett.*, *29*(16), 1757, doi:10.1029/2001GL014029.

Narita, H., M. Sato, S. Tsunogai, M. Murayama, M. Ikehara, T. Nakatsuka, M. Wakatsuchi, N. Harada, and Y. Ujiié (2002), Biogenic opal indicating less productive northwestern North Pacific during the glacial ages, *Geophys. Res. Lett.*, *29*(15), 1732, doi:10.1029/2001GL014320.

Ohkouchi, N., K. Kawamura, and A. Taira (1997), Fluctuations of terrestrial and marine biomarkers in the western tropical Pacific during the last 23,300 years, *Paleoceanography*, *12*, 623–630.

Petit, J. R., et al. (1999), Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature*, *399*, 429–436.

Prahl, F. G., and S. G. Wakeham (1987), Calibration of unsaturation patterns in long-chain ketone compositions for paleotemperature, *Nature*, *330*, 367–369.

Prahl, F. G., L. A. Muehlhausen, and M. Leyle (1989), An organic geochemical assessment of oceanographic conditions at MANOP site C over the past 26,000 years, *Paleoceanography*, *4*, 495–510.

Rechka, J. A., and J. R. Maxwell (1988), Characterization of alkenone temperature indicators in sediments and organisms, *Org. Geochem.*, *13*, 727–734.

Richter, B. E. (2000), Extraction of hydrocarbon contamination from soils using accelerated solvent extraction, *J. Chromatogr. A*, *874*, 217–224.

Riegman, R., A. A. M. Noordeloos, and G. C. Cadée (1992), *Phaeocystis* blooms and eutrophication of the continental coastal zones of the North Sea, *Mar. Biol.*, *112*, 479–484.

Riegman, R., W. Stolte, A. A. M. Noordeloos, and D. Slezak (2000), Nutrient uptake and alkaline phosphate (EC 3:1:3:1) activity of *Emiliania huxleyi* (*Prymnesiophyceae*) during growth under N and P limitation in continuous cultures, *J. Phycol.*, *36*, 87–96.

Robinson, N., G. Eglinton, S. C. Brassell, and P. A. Cranwell (1984), Dinoflagellate origin for sedimentary 4α-methylsteroids and 5α(H)-stanols, *Nature*, *308*, 439–442.

Robinson, N., P. A. Cranwell, G. Eglinton, and G. H. M. Jaworski (1987), Lipids of four species of freshwater dinoflagellates, *Phytochemistry*, *26*, 411–421.

Sakamoto, T., T. Tanabe, and H. Shimizu (2001), Millennium-scale rapid and intensive cooling events and sea ice history in the Okhotsk Sea, paper presented at *7th International Conference on Paleoceanography*, Palaeontol. Soc. of Jpn., Sendai, Japan.

Sarmiento, J. L., and J. R. Toggweiler (1984), A new model for the role of the oceans in determining atmospheric P$_{CO2}$, *Nature*, *308*, 621–624.

Seki, O., K. Kawamura, T. Nakatsuka, K. Ohnishi, M. Ikehara, and M. Wakatsuchi (2003), Sediment core profiles of long-chain n-alkanes in the Sea of Okhotsk: Enhanced transport of terrestrial organic matter from the last deglaciation to the early Holocene, *Geophys. Res. Lett.*, *30*(1), 1001, doi:10.1029/2001GL014464.

Seki, O., K. Kawamura, M. Ikehara, T. Nakatsuka, and T. Oba (2004), Variation of alkenone sea surface temperature in the Sea of Okhotsk over the last 85 kyrs, *Org. Geochem.*, in press.

Shackleton, N. J. (1977), Carbon-13 in *Uvigerina*: Tropical rainforest history and equatorial Pacific carbonate dissolution cycles, in *The Fate of Fossil Fuel CO$_2$ in the Oceans*, edited by N. R. Anderson and A. Malahoff, pp. 401–427, Plenum, New York.

Shiga, K., and I. Koizumi (2000), Latest Quaternary oceanographic changes in the Okhotsk Sea based on diatom records, *Mar. Micropaleontol.*, *38*, 91–117.

Shiga, K., I. Koizumi, M. Ikehara, T. Nakatsuka, and M. Wakatsuchi (2001), Changes of the diatom assemblage and marine surface environment in the Okhotsk sea during the last 125,000 years, paper presented at *7th International Conference on Paleoceanography*, Palaeontol. Soc. of Jpn., Sendai, Japan.

Sicre, M.-A., Y. Ternois, M. Paterne, A. Boireau, L. Beaufort, P. Martinez, and P. Bertrand (2000), Biomarker stratigraphic records over the last 150 kyrs off the NW African coast at 25°N, *Org. Geochem.*, *31*, 577–588.

Sicre, M.-A., Y. Ternois, M. Paterne, P. Martinez, and P. Bertrand (2001), Climatic changes in the upwelling region off Cap Blanc, NW Africa, over the last 70 kyr: A multi-biomarker approach, *Org. Geochem.*, *32*, 981–990.

Siegenthaler, U., and T. Wenk (1984), Rapid atmospheric CO_2 variations and ocean circulation, *Nature*, *308*, 624–626.

Simmield, G. B., S. Derrick, A. Mackensen, H. Grobe, and C. Pudsey (1994), The history of barium, biogenic silica and organic carbon accumulation in the Weddell Sea and Antarctic Ocean over the last 150,000 years, in *Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change*, edited by R. Zahn et al., pp. 555–574, Springer-Verlag, New York.

Stuiver, M., P. J. Reimer, E. Bard, J. W. Beck, G. S. Burr, K. A. Hughen, B. Kromer, G. McCormac, J. van der Plicht, and M. Spurk (1998), INTCAL98 radiocarbon age calibration, 24,000-0 cal BP, *Radiocarbon*, *40*, 1041–1083.

Sun, M.-Y., and S. G. Wakeham (1994), Molecular evidence for degradation and preservation of organic matter in the anoxic Black Sea Basin, *Geochim. Cosmochim. Acta*, *58*, 3395–3406.

Takahashi, K. (1998), The Bering and Okhotsk Seas: Modern and past paleoceanographic changes and gateway impact, *J. Asian Earth Sci.*, *16*, 49–58.

Takahashi, K., N. Fujitani, M. Yanada, and Y. Maita (1997), Five year long particle fluxes in the central subarctic Pacific and the Bering Sea, in *Biogeochemical Processes in the North Pacific*, edited by S. Tsunogai, pp. 277–289, Jpn. Mar. Sci. Found., Tokyo.

Takahashi, K., N. Fujitani, M. Yanada, and Y. Maita (2000), Long-term biogenic particle fluxes in the Bering Sea and central subarctic Pacific Ocean, 1990–1995, *Deep Sea Res. Part I*, *47*, 1723–1759.

Talley, L. D. (1991), An Okhotsk Sea water anomaly: Implication for ventilation in the North Pacific, *Deep Sea Res.*, *38*, 171–190.

Ternois, Y., M.-A. Sicre, and M. Paterne (2000), Climatic changes along the northwestern African continental margin over the last 30 kyr, *Geophys. Res. Lett.*, *27*, 133–136.

Ternois, Y., K. Kawamura, L. D. Keigwin, N. Ohkouchi, and T. Nakatsuka (2001), A biomarker approach for assessing marine and terrigenous inputs to the sediments of Sea of Okhotsk for the last 27,000 years, *Geochim. Cosmochim, Acta*, *65*, 791–802.

Velichko, A. A., M. Kononov, and M. A. Faustova (1997a), The last glaciation of earth: Size and volume of ice-sheets, *Quat. Int.*, *41/42*, 43–51.

Velichko, A. A., A. A. Andreev, and V. A. Klimanov (1997b), Climate and vegetation dynamics in the tundra and forest zone during the late glacial and Holocene, *Quat. Int.*, *41/42*, 71–96.

Villanueva, J., J. O. Grimalt, E. Cortijo, L. Vidal, and L. Labeyrie (1997), A biomarker approach to the organic matter deposited in the North Atlantic during the last climatic cycle, *Geochim. Cosmochim. Acta*, *61*, 4633–4646.

Volkman, J. K. (1986), A review of sterol markers for marine and terrigenous organic matter, *Org. Geochem.*, *9*, 83–100.

Vörösmarty, C. J., B. Fekete, and B. A. Tucker (1998), *River Discharge Database, Version 1*, RivDIS.V1.0 suppl., Inst. for the Study of Earth, Oceans, and Space, Univ. of N. H., Durham, N. H. (Available at http://www.watsys. unh.edu/)

Wong, C. S., F. A. Whitney, I. Tsoy, and A. Bychkov (1995), The opal pump and subarctic carbon removal, in *Global Fluxes of Carbon and Its Related Substances in the Coastal Sea-Ocean-Atmosphere System, Proceedings of the 1994 Sapporo IGBP Symposium*, edited by S. Tsunogai et al., pp. 339–344, M & J Int., Yokohama, Japan.

Yokoyama, Y., K. Lambeck, P. De Deckker, P. Johnston, and L. K. Fifield (2000), Timing of the last glacial maximum from observed sea-level minima, *Nature*, *406*, 713–716.

Zahn, R., A. Rushdi, N. G. Pisias, B. D. Bornhold, B. Blaise, and R. Karlin (1991), Carbonate deposition and benthic 13C in Subarctic Pacific: Implications for changes of the oceanic carbonate system during the past 750,000 years, *Earth Planet. Sci. Lett.*, *103*, 116–132.

Zhao, M., G. Eglinton, S. K. Haslett, R. W. Jordan, M. Sarnthein, and Z. Zhang (2000), Marine and terrestrial biomarker records for the last 35,000 years at ODP site 658C off NW Africa, *Org. Geochem.*, *31*, 919–930.

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