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Carbon isotope variations in diploptene for methane hydrate dissociation during the last glacial episode in the Japan Sea/East Sea

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Two piston cores (06GHSA P1 and 06GHSA P6) taken from the Ulleung Basin of the Japan Sea/East Sea were examined for the presence of an organic compound, diploptene (hopanoid 17α(H),21β(H)-hop-22(29)-ene). Carbon isotopes of diploptene ($\delta^{13}C_{dip}$) were analyzed to determine their origins and relationship with methane hydrate dissociation.

The presence of diploptene was identified, and its concentrations in the two cores exhibited spatiotemporal variations, ranging from 1.7 to 632.1 ng/g (average, 87 ng/g) in core 06GHSA P6 and from 1.4 to 42.2 ng/g in core 06GHSA P1 (average, 20.1 ng/g). In both cores, $\delta^{13}C_{dip}$ exhibited significant variations, ranging from –22.3 to –61.3‰. In core 06GHSA P6, extreme $\delta^{13}C_{dip}$ depletion was evident in the sediments deposited under glacial conditions, whereas relatively enriched values were determined in Holocene sediments. High diploptene concentrations correspond to depleted $\delta^{13}C_{dip}$, indicating that carbon was, in part, derived from methanotrophic bacterial activities, whereas low diploptene concentrations may reflect a mainly cyanobacterial origin. The presence of depleted $\delta^{13}C_{dip}$ and its fluctuation may record the dissociation of gas hydrates and methane seepage during glacial intervals for core 06GHSA P6.

The release of methane hydrate release may have been triggered by the collapse of the stability zone. Several factors associated with the hydrate stability include sea-level fluctuations. Lowered sea levels during glacial periods may cause the collapse of hydrate stability zone, which could be the source of dissociated of methane hydrate and methane seepage. This study documents the evidence of methane hydrate instability, inferred from compound-specific analysis, of the Japan Sea/East Sea sediments.

Keywords: diploptene, methane hydrate dissociation, carbon isotope, glacial–interglacial, sea-level changes

INTRODUCTION

Methane hydrates preserved in marine sediments are of interest both as potential for future energy resources and as a controlling factor for past climate changes (Kennett *et al.*, 2000; Max, 2003). In particular, methane hydrate instability and episodic methane gas emissions into the water column and atmosphere are clearly related to environmental changes over geological time scales (Kennett and Stott, 1991; Dickens *et al.*, 1995; Padden *et al.*, 2001; Archer, 2007). Although atmospheric methane has been attributed predominantly to emissions from natural wetlands, volumetrically impressive emissions into the marine water column, and eventually into the atmosphere, are now known to originate from deep-sea sediments (Kennett *et al.*, 2000; Garidel-Thoron *et al.*, 2004). Focused studies on methane hydrate dissociation, anaerobic oxidation of methane (AOM), and seepage into the water column, and its effects on global climate, have been conducted in various regions (Kennett *et al.*, 2000; Hinrichs *et al.*, 2003; Uchida *et al.*, 2004; Raghoebarsing *et al.*, 2006).

The organic compound diploptene is commonly a major constituent of hydrocarbons. It is common in marine sediments and can be used as a proxy for methane hydrate dissociation (Prahl *et al.*, 1992; Yamada *et al.*, 1997). This biomarker represents one of the best approaches to identify methane emissions from deep-sea sediments (Elvert *et al.*, 2001; Hinrichs *et al.*, 2003;

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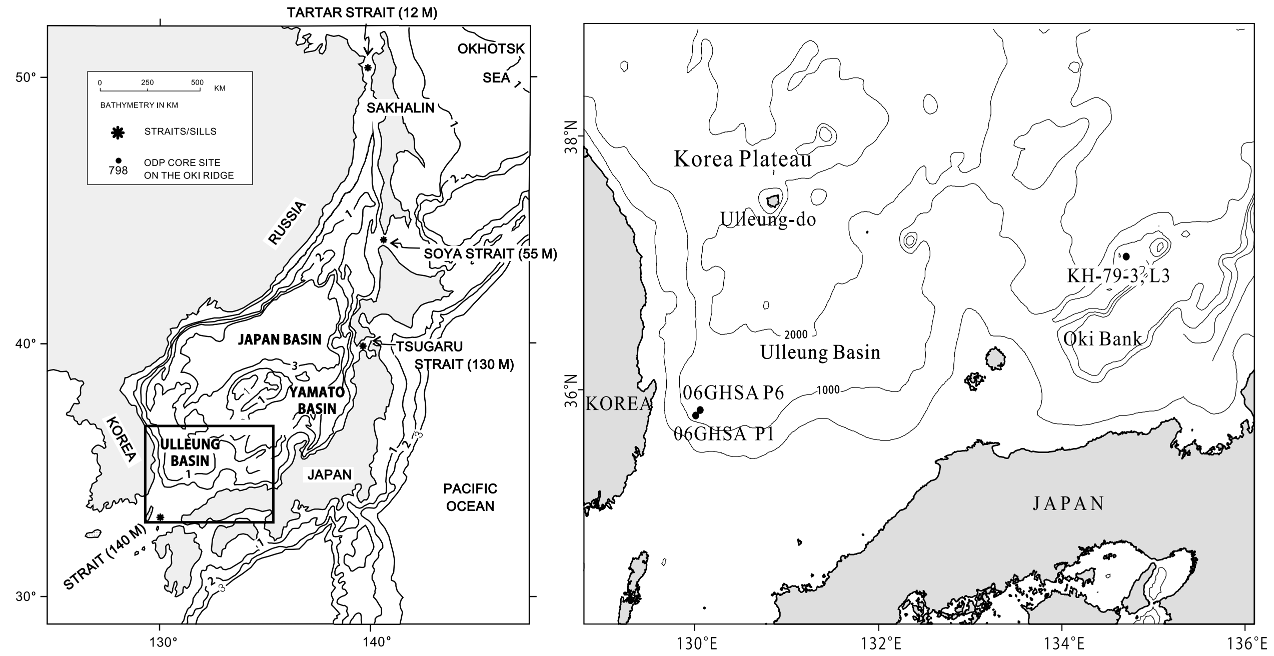

Fig. 1. Physiographic map and bathymetry of the Japan Sea/East Sea and surrounding areas. Core locations are shown by black dots (water depth is shown in meters). A dot near the Oki bank indicates the core location of Yamada et al. (1997).

Uchida *et al.*, 2004). Although diploptene has been associated with both cyanobacteria and methanotrophic bacteria, the most important source of diploptene in marine sediments has been considered to be aerobic methanotrophic bacteria in methane-related environments (Yamada *et al.*, 1997; Elvert *et al.*, 2001; Uchida *et al.*, 2004). Tracking methane hydrate dissociation and resultant seepage into the water column, as a result of gas hydrate stability zone collapse, requires that the seeped carbon be characterized by using carbon isotope signatures of diploptene and carbonates, such as foraminifera or authigenic carbonates (Pape *et al.*, 2005; Chen *et al.*, 2007; Nam and Lee, 2009; Nehza *et al.*, 2012).

Although the presence of methane hydrates and their dissociation and seepage to the sea floor have been confirmed in areas such as the Santa Barbara Basin, the northwest Pacific Ocean, and in the Japan Sea/East Sea (Kennett *et al.*, 2000; Uchida *et al.*, 2004; Bahk *et al.*, 2009), the processes involved in this phenomenon are not well understood. Hydrate dissociation is explained by the incursion of warm intermediate water during interstadial periods in the Santa Barbara Basin and North Pacific areas, but not in the Japan Sea/East Sea. This study focuses on diploptene and its carbon isotope variation as a possible proxy for methane hydrate dissociation in sedimentary environments of the Japan Sea/East Sea, and investigates the processes and paleoceanographic effects associated with hydrate dissociation.

Regional Setting

Japan Sea/East Sea is a marginal sea and a well-known back-arc basin of the Eurasian continent. It comprises three major deep oceanic basins, the Ulleung, Yamato, and Japan basins (Fig. 1). The Ulleung Basin is located in the southern part of the Japan Sea/East Sea, and is connected with the East China Sea through the Korea Strait to the south. The Ulleung Basin is a bowl-shaped basin with a maximum water depth of approximately 2,200 m. It is bounded by the steep continental slope of the eastern Korean Peninsula to the west. The southern part of the Ulleung Basin, at the entrance to the Korea Strait, has a sill depth of approximately 140 m, and this shallow depth may have been critical to the Ulleung Basin's paleoceanographic history because sea-level lowering during past glacial periods could be as low as approximately 120–130 m (Fairbanks, 1989).

The sea floor of the Ulleung Basin is relatively flat, with a very gentle slope in its southern part. Sediment thickness is approximately 4 km throughout of the basin, but reaches about 10 km in the southern part (Lee *et al.*, 2001). Previous research has identified widespread mass failure deposits in the southern part of the basin (Lee *et al.*, 1999). The high sedimentation rate from the gentle slope of the southern part of Ulleung Basin can provide valuable high-resolution geochemical records, and may provide favorable conditions for gas hydrate exploration.

A seismic survey to detect natural gas hydrate in the Japan Sea/East Sea was conducted (Gardner *et al.*, 1998), and acoustic imaging was focused in the Ulleung Basin (Lee *et al.*, 2005; Yoo *et al.*, 2008). Methane in the nearby, shallow-water part of the South Sea of Korea is known to be a mixture of biogenic and thermogenic origins (Jeong *et al.*, 2004). Methane hydrates have been discovered at very shallow sediment depths in the northeastern part of the Japan Sea/East Sea, on the Umitaka Spur of the Joetsu Basin (Hiruta *et al.*, 2009). These discoveries suggest that methane hydrate could be present in the marginal basins of the Japan Sea/East Sea.

MATERIALS AND METHODS

Sampling, core lithology, and age determination

Two piston cores (06GHSA P1 and 06GHSA P6) were collected from the southwestern part of the Ulleung Basin, Japan Sea/East Sea during the 2006 cruise for assessment of hydrate-related geohazard potential (Fig. 1). Each core was described sedimentologically and then X-rayed to highlight detailed sedimentary structures (KIGAM, 2007). The results of these three methods were combined to identify sedimentary facies (Fig. 2). A well-known characteristic of the Japan Sea/East Sea sediments deposited during glacial intervals is a presence of laminations, which is a sedimentary structure that helps to identify the muds deposited during glacial periods (core 06GHSA P6 only). In particular, these thick dark laminated mud intervals in the lower part of the core have been related to significant sea-level lowering during glacial periods which might have resulted in restricted deep-water circulation and basin-wide correlation in the Japan Sea/East Sea (Bahk *et al.*, 2000; Khim *et al.*, 2009).

Cores were sampled at 1–4 cm intervals for geochemical analyses, such as total organic carbon (TOC), carbon and nitrogen isotopes of organic matter, and diploptene content. To link geochemical variations to a time-frame, ^{14}C dating was conducted using foraminiferal tests at the Rafter Radiocarbon Laboratory in New Zealand. In the core 06GHSA P1, ^{14}C carbon ages were conducted on the sediments from the 107 cm and 364 cm core depths, corresponding to 2,322 and 3,968 years before the present, indicating that this part of the core is Holocene sediment. Three samples from the core 06GHSA P6 (541 cm, 586 cm, and 675 cm core depths) yielded the dates of 10,310, 14,609 and 18,118 years before present (BP), indicating that this core contains glacial sediment at its base (KIGAM, 2007). Accelerator mass spectrometry (AMS) absolute ages were transformed to calendar ages using the CAIB 5.0 program. Detailed lithology and ^{14}C age results are presented in Table 1 and Fig. 2.

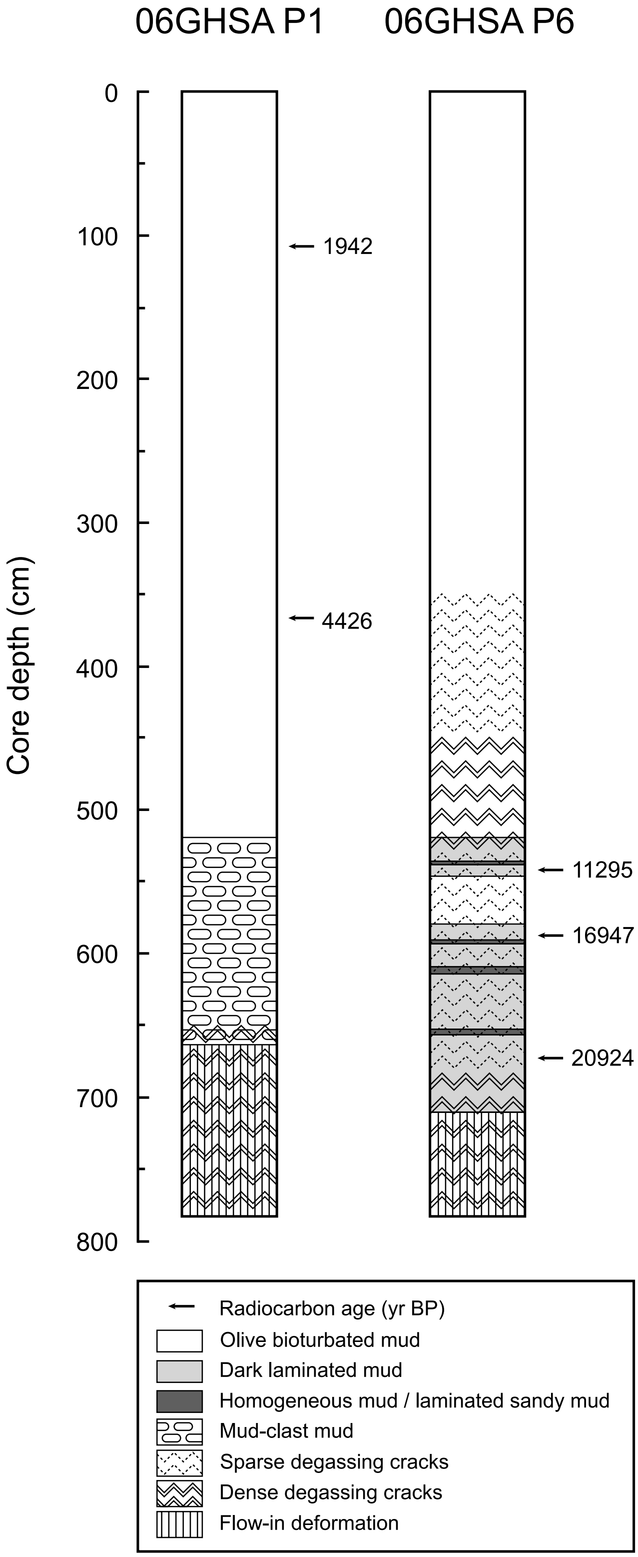

Fig. 2. Lithologic variations in the cores 06GHSA P1 and P6. Arrows on the right side of each lithology column indicate calendar ages in years before present (BP) based on ^{14}C age. Cracks due to shallow gas expansion and deformed intervals during coring are also denoted.

Table 1. Location, water depth and other information used in this study. Summarized core lithology and accelerator mass spectrometry (AMS) age dates are illustrated (modified from KIGAM, 2007)

Core ID	Latitude (N)	Longitude (E)	Water depth (m)	AMS layers	AMS ages (Cal.)	Summarized lithology
06GHSA P1	35°47.7119	130°0.9404	1083	107	1942 ± 30	bioturbated mud
				364	4426 ± 30	mud-clast mud
06GHSA P6	35°50.3191	130°3.6800	1189	541	11295 ± 40	biotrubated mud
				586	16947 ± 55	laminated mud
				675	20924 ± 70	sparse degassing cracks
KH-79-3, L3	37°03.5′	134°42.6′	935	9 layers	No correction	bioturbated mud
				Yamada *et al.* (1997)		several volcanic layers

Total organic carbon and stable isotopes of carbon and nitrogen

Bulk sediment samples were conducted to measure total carbon (TC) and total organic carbon (TOC) contents using a CHNS analyzer at the Korea Institute of Ocean Science and Technology (KIOST). Powdered sediments treated by an agate motor to measure for TC content was first determined by direct measurement after dry on 60°C. TOC contents were determined by analyzing powdered samples treated with 1 N HCl. The amount of carbonate was calculated from the weight difference between TC and TOC expressed as weight % of calcium carbonate content (CaCO$_3$ %) = (TC wt. % – TOC wt. %)$*$(100/12). C/N ratio (total organic carbon/total nitrogen) of the organic matter was also calculated from the calculated result to trace the source of the organic matter (Stein, 1990).

To determine the nature of organic matter, stable carbon (^{13}C$_{org}$) and nitrogen (^{15}N$_{org}$) isotopes of organic matter were measured by using CF-IRMS (continuous flow isotope ratio mass spectrometer) at the Seoul National University. Analytical errors for TOC and TC are less than 5% based on duplicated analysis. The analytical errors of ^{13}C$_{org}$ and ^{15}N$_{org}$ are assumed to be less than 5%.

Extraction and detection of diploptene and its concentration

Approximately 10 g of core samples from each analytical horizon were extracted with an accelerated solvent extractor (ASE 200, Dionex Korea Ltd., Seoul, Korea) at 100°C and 1500 psi for 15 min. The solvents were a mixture of distilled dichloromethane and methanol (99:1 v/v). Before the extraction, the internal standard (o-terphenyl) was added for checking recovery of target compounds. The lipid extract was separated into four fractions (F1: 3 ml of hexane; F2: 3 ml of hexane–toluene (3:1); F3: 4 ml of toluene; and F4: 3 ml of toluene–methanol (3:1)) by column chromatography (SiO$_2$ with 5% distilled water; i.d., 5.5 mm; length, 45 mm). Diploptene was analyzed by the modified method of Uchida *et al.* (2004).

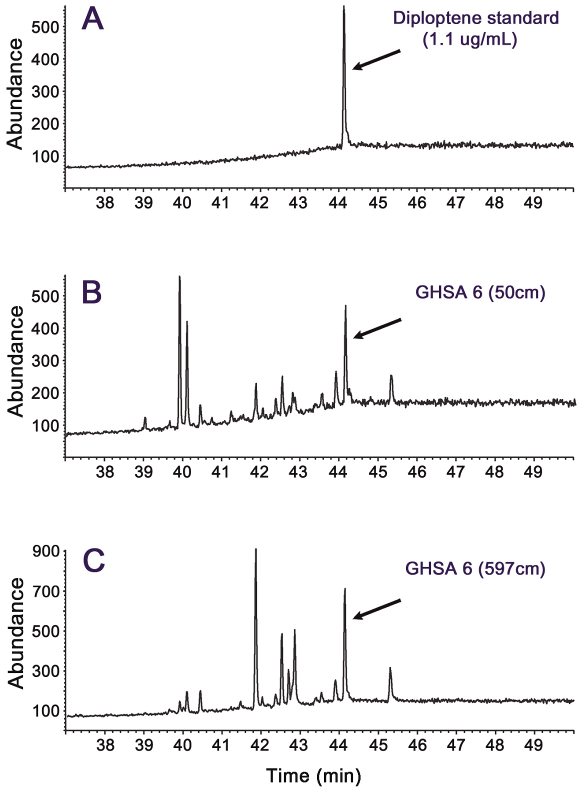

Fig. 3. Chromatograms of diploptene standard (A) and unknown core samples (B and C) monitored at m/z 191. Identification and quantification of diploptene were made using authentic standard. Diploptene appeared at a retention times of 44.14 min.

Gas chromatography of the F1 fraction was conducted using a Hewlett-Packard (HP) 5890 series II gas chromatograph (GC) with mass spectrometry (Agilent 5792,

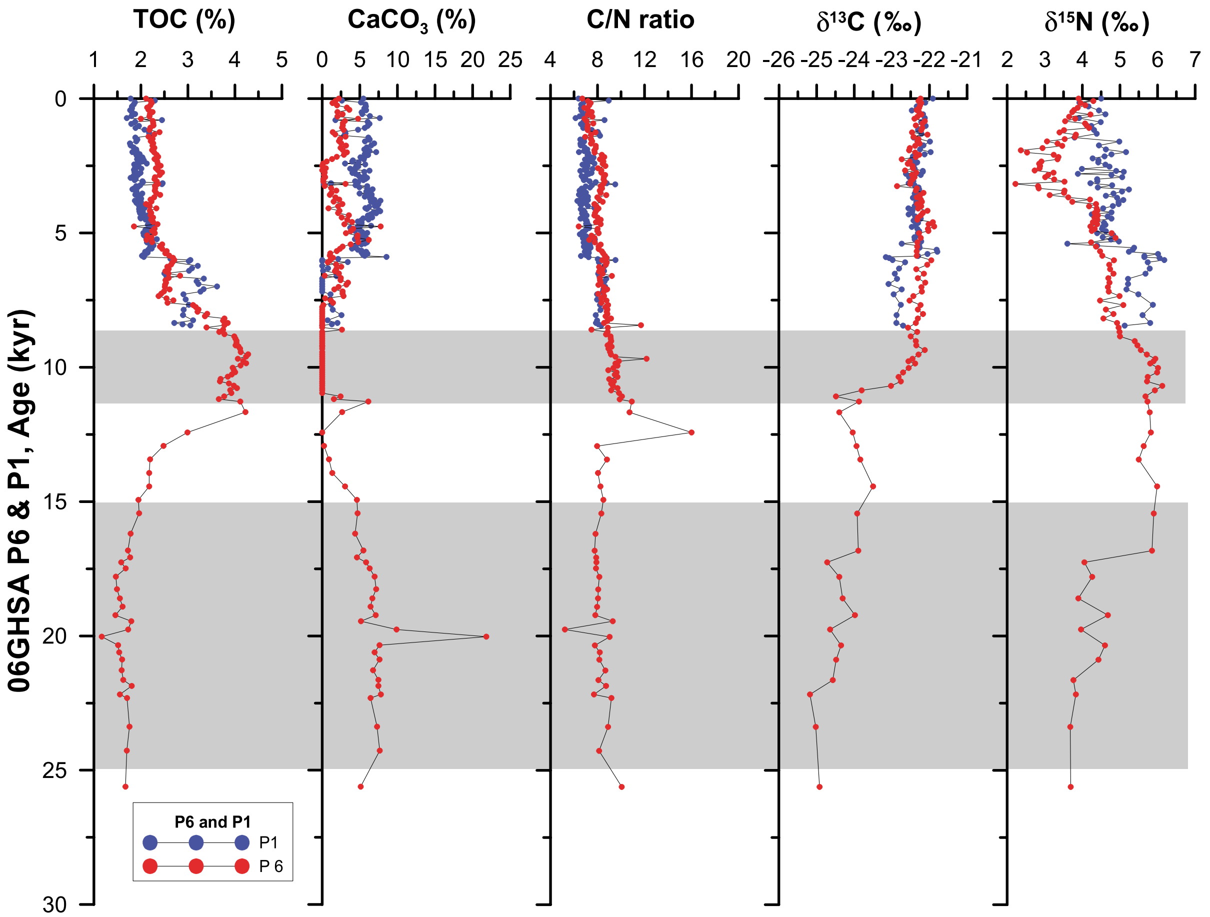

Fig. 4. Total organic carbon (TOC), carbonate content and C/N ratio of the organic matter. δ^{13}C and δ^{15}N values of organic matter from the cores 06GHSA P6 and 06GHSA P1 are illustrated. Shaded areas indicate the glacial intervals.

USA). A 30 m × 0.25 mm I.D. DB-5MS capillary column (J&W Scientific, USA) was used. The injector temperature was set at 300°C and the transfer line at 280°C. The initial temperature program of the GC oven was set at 60°C for 1.5 min; first rate at 4°C/min to 300°C; and the isothermal pause at 300°C for 10 min. Helium was used as a carrier gas, and electron impact spectra were obtained at 70 eV. Compound identification was achieved by comparison of its mass spectra and retention times with authentic standard (Chiron, Norway). Ion *m*/*z* 191 was selected for quantitation of diploptene and ion *m*/*z* 410 for confirmation. Because *m*/*z* 191 is generally a characteristic of hopanoids, it is crucial to identify diploptene not only by the mass fragments but by retention times, as well. Examples of the chromatogram's results on standard and unknown samples were shown in Fig. 3.

Carbon isotopes in diploptene

Stable carbon isotope ratios of diploptene ($\delta^{13}C_{dip}$) were determined by isotope ratio monitoring gas chromatography-combustion-isotope ratio mass spectrometry (GC/C/IRMS) with a system consisting of an HP6890 GC and a Finnigan MAT252 at the National Institute of Environmental Study (NIES), in Japan. Carbon isotope compositions were reported using δ notation as per mil deviations from the Pee Dee Belemnite Standard (PDB). Pre-treatment of samples and analytical methods were those of Uchida *et al*. (2004).

RESULTS AND DISCUSSION

TOC contents of the analyzed cores varied from 1.17% to 4.28% in the core 06GHSA P6 and from 3.62% to 1.78% in the core 06GHSA P1. Carbonate contents of two cores varied from 0 to 21.8%, showing generally high during glacial and lower during the Holocene. Carbon and nitrogen levels in organic matter show high fluctuation during glacial and interglacial periods. Depleted $\delta^{13}C_{org}$ values (approximately –24 ~ –25‰) were present between 25~10 ka and it levels vary within –22 ~ –23‰ during the Holocene with a pronounced shift between approximately 8 ka and 10 ka in the core of 06GHSA P6. An organic compound of diploptene concentration shows extreme changes between the Holocene and glacial sediment. Concentration of diploptene is generally higher during glacial period and lower during the Holocene. Its carbon isotopic value is enriched during the Holocene and depleted in glacial aged sediments. Analytical results of the diploptene and its carbon isotope with other geochemical data ($^{13}C_{org}$ and $^{15}N_{org}$) are shown in Figs. 3 and 4.

Vertical variations in core sediments and geochemical proxies

Sediments deposited in deep-sea environments record paleoenvironmental changes in overlying water columns and at the sediment-water interface. Detailed examination of the cores in this study indicates that sediments are mostly composed of clays, organic matter, and carbonates. Grain-size analysis of both cores indicated generally hemipelagic compositions with *ca*. 70–80% silt (Fig. 2). Core 06GHSA P1 contains bioturbated mud throughout, whereas core 06GHSA P6 contains bioturbated mud in its upper part and laminated mud below. The dark laminated mud (DLM) is interpreted as hemipelagite that was deposited under anaerobic bottom conditions during the Last Glacial Maximum (LGM) (Bahk *et al*., 2000), when sea level was 120 m lower than its present position.

Organic matter is the source of oil and gas in deep-sea environments. In this context, knowing the amount, and source of organic matter provide valuable information for oil and methane hydrate exploration, and the content of total organic carbon (TOC) is regarded as an important component (Max, 2003). TOC contents of the analyzed cores varied from 1.17% to 4.28% in core 06GHSA P6 and from 3.62% to 1.78% in core 06GHSA P1 (Fig. 4). TOC contents of core 06GHSA P6 were elevated between 12 ka and 8 ka, which may indicate increased productivity during that interval. In core 06GHSA P6, the elevated TOC interval was associated with a TOC versus organic nitrogen (C/N) ratio of <10 in most layers, except for several peaks in transitional intervals, during which allochthonous terrigenous organic matter may have been delivered (Stein, 1990). Considering previous studies, TOC contents are not insufficient for the formation of oil and gas hydrates.

Carbonate contents of the two cores varied from 0 to 21.8%, showing glacial/interglacial fluctuations. Carbonate content was almost zero in the high-TOC interval, between 12 ka and 8 ka in core 06GHSA P6 (Fig. 4). Carbonate content is controlled by carbonate productivity, carbonate dissolution, and dilution by terrigenous materials. The carbonate-barren intervals in these cores are probably associated with carbonate dissolution because carbonate compensation depth (CCD) of the Japan Sea/East Sea currently lies at an approximate water depth of 1,500 m (Ujiie and Ichikura, 1973). In this studied core, 06GHSA P1 does not include DLM, but 06GHSA P6 contains numerous DLM layers that correspond to dark laminated sediment (DLS). The majority of depleted carbonate contents of core 06GHSA P6 (almost zero) between 12–8 ka corresponded to a DLS layer that was deposited under anaerobic bottom-water conditions (Fig. 4). However, an higher carbonate interval occurred during the glacial period, which may reflect enhanced biogenic carbonate preservation and/or productivity or growth of authigenic carbonate originated from methane gas seepage (Nehza *et al*., 2012). Detailed investigation of core sediments by soft X-rays did not reveal carbonate nodules. The increased carbonate content in the two cores was probably supplied by planktonic microfossils. However, judging from the occurrence of authigenic micro carbonate nodules from nearby core sediments (Bahk *et al*., 2009), authigenic carbonates may be formed by methane gas seepage into anaerobic bottom water.

Carbon and nitrogen isotopic values of organic matter ($\delta^{13}C_{org}$, $\delta^{15}N_{org}$) are used to characterize the source of organic materials and associated paleoenvironmental changes (Lehmann *et al*., 2002). $\delta^{13}C_{org}$ values of marine planktons are approximately –20‰, whereas those from terrestrial plants are typically ~5–10‰ lower than marine values. Variability in $\delta^{13}C_{org}$ can, therefore, provide valuable information about the source of organic material. Core 06GHSA P6 exhibited average $\delta^{13}C$ values of –22.69‰ and $\delta^{15}N$ values of 4.3‰ ($n = 117$), but $\delta^{13}C_{org}$ exhibited a pronounced shift between about 8 and 10 ka. Above this interval (Holocene), it was between –23 and –22‰, but values were much more negative below. Depleted carbon isotope values in sediments older than 12 ka indicate dilution of *in situ* organic matter by terrigenous organic materials, and this interpretation appears to be supported by the C/N ratio. Nitrogen isotope compositions of organic matter changed at 16 ka and, subtly, at 6 ka (Fig. 4). Comparing these results with the aforementioned carbon data, strongly enriched $\delta^{15}N$ values between 16 ka and 9 ka correlate with the increasing trend of TOC, possibly indicating enhanced productivity.

Source and distribution of diploptene

The hopanoid biomarker diploptene is present in diverse recent and ancient sedimentary environments. It is thought to be derived from bacterial activities and is readily preserved in deep-sea sediments. In particular, methane concentrations in sediment are known to be associated through the processes of anaerobic oxidation of methane (AOM), which is critical in the reduction of the greenhouse gas methane from the ocean into the atmosphere. A recent study indicated that AOM is mediated by a

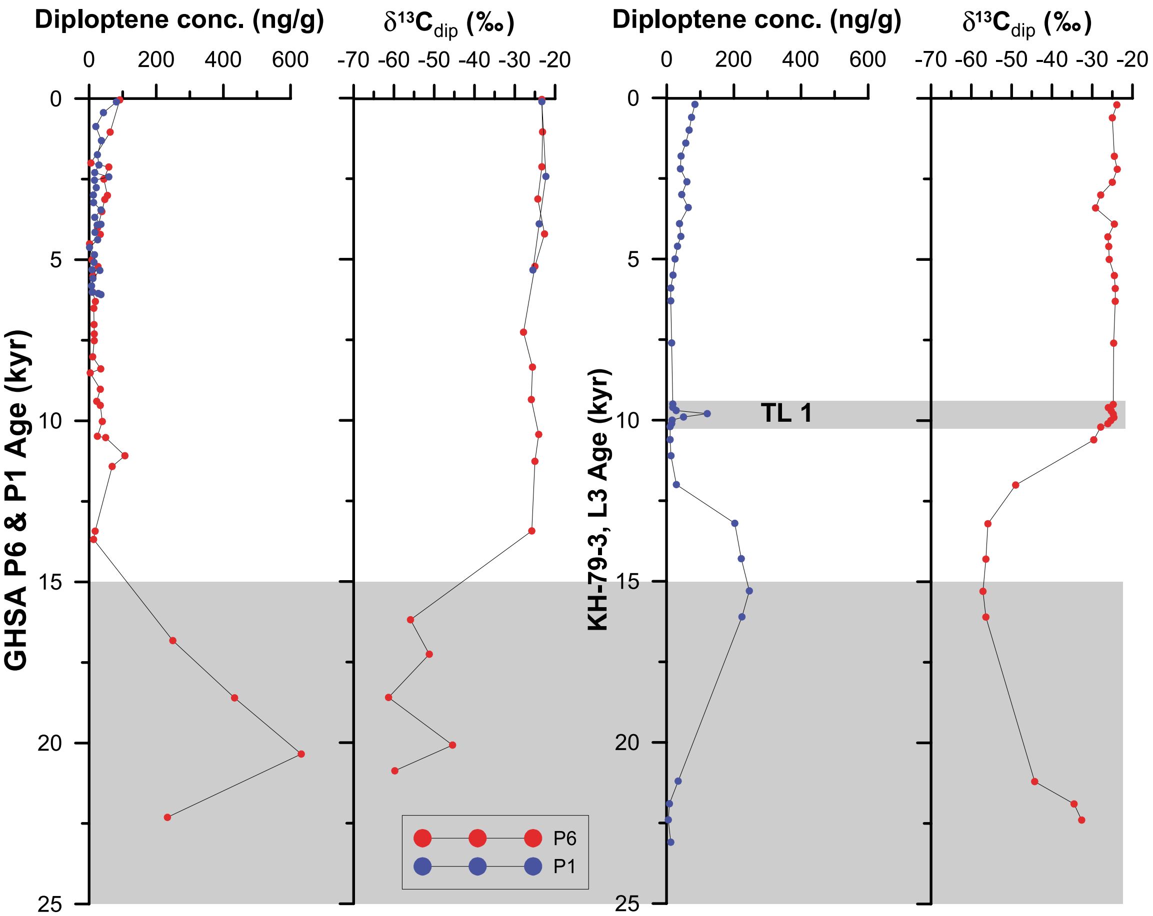

Fig. 5. Vertical variations in diploptene concentrations and its carbon isotopic values of the two cores (left two figures). Diploptene concentrations and their carbon isotope values are compared with those of Yamada et al. (1997). Shaded areas indicate glacial intervals. TL denotes a thin laminated layer.

syntrophic consortium of methanotrophic archaea and sulfate-reducing bacteria (Raghoebarsing *et al.*, 2006). Within this theory, diploptene derived from methanogenesis is critical in tracking the past behavior of methane emissions.

In previous studies, diploptene abundance is known to reflect glacial–interglacial cycles (Prahl *et al.*, 1992; Elvert *et al.*, 2001). Diploptene is commonly produced by bacterial activities in bottom-water and at oxic-anoxic interfaces, and therefore, its distribution may reflect environmental changes. Methanotrophic bacteria consume methane that was produced by the dissociation of methane hydrate, and the diploptene produced during this process exhibits highly depleted carbon isotopic values (Uchida *et al.*, 2004; Hinrichs *et al.*, 2003). Recent studies show that high levels of diploptene concentration and extremely depleted carbon isotope values indicate an association with methane hydrate dissociation, and the extremely light carbon isotope signature is passed on to calcareous benthic organisms (Kennett *et al.*, 2000; Cannariato and Stott, 2004; Uchida *et al.*, 2004).

Within the two cores, diploptene concentrations show striking variations (Fig. 5). In core 06GHSA P1 and the upper part of 06 GHSA P6 core (~14 ka), it did not exceed 100 ng/g, however, in LGM sediments of core 06GHSA P6, it exceeded 600 ng/g. To understand the elevated diploptene concentrations during the glacial interval, carbon isotopes of diploptene ($\delta^{13}C_{dip}$) were analyzed from samples throughout the cores, and they show strong time-dependent variations. During the Holocene and the transitional interval, carbon isotope values were between –20 and –30‰, whereas lighter values, reaching as low as about –60‰, were present in LGM sediments from core 06GHSA P6 (Fig. 5). In core 06GHSA P1 (Holocene only), the values were between –20 and –30‰, and showed no significant variation.

A similar study of diploptene organic geochemistry and paleoenvironmental change was conducted on sediments from Saanich Inlet, where distinct differences in the diploptene content of Holocene and earlier sediments were evident (Elvert *et al.*, 2001). The concentration of diploptene increased abruptly at ~6000 years. Carbon isotope records from this interval reflect changes in the microbial community structure of bacteria living at the oxic-anoxic interface, whereas carbon isotope values of sediments older than ~6,000 years, reaching –26.3‰, can be attributed to planktonic cyanobacteria.

Organic compound analyses were conducted on Japan Sea/East Sea sediments by Ishiwatari *et al.* (1994) and Yamada *et al.* (1997). In these studies, diploptene concentrations fluctuated widely throughout the glacial and interglacial intervals, and exhibited a steep increase during the LGM, between 15 ka and 18 ka (Yamada *et al.*, 1997). Strongly depleted diploptene carbon isotopic values (approximately –55‰) characterized this interval, resembling the results of the current study (Fig. 5). Diploptene concentrations and diploptene carbon isotopic values defined two groups, which were interpreted as the products of various diploptene synthesis mechanisms. In Holocene sediments, which contain both lower diploptene concentrations and enriched carbon isotope values, diploptene was interpreted to be of cyanobacterial origin. Older sediments contained high diploptene concentrations and depleted diploptene carbon isotopic values, which were attributed to methanotrophic bacteria. These bacteria were thought to have flourished during glacial intervals owing to the development of sea-water stratification and deep-water anoxia during periods of lowered sea levels. The slight increase in diploptene concentration in the TL1 layer of Yamada *et al.* (1997) (Fig. 5), may have resulted from increased cyanobacterial activity, because the carbon isotopic values of diploptene remain in the range of –20 to –30‰.

Carbon isotopic compositions of the diploptene that formed during glacial intervals clearly differed from those of the Holocene sediments, demonstrating that this biomarker records paleoenvironmental variations. Strongly depleted carbon isotopic values from approximately –60 to –50‰ may result from bacterial activities during methane hydrate dissociation, whereas relatively enriched carbon isotopic values in Holocene sediments may be derived from cyanobacterial sources. Therefore, strongly negative carbon isotopic values thus suggest methane seepage, due to methane hydrate dissociation during the LGM in core 06GHSA P6 (Fig. 5).

Strongly depleted carbon isotopic values have been reported from the tests of benthic foraminifers, which may have been directly affected by seep-associated methane (Kennett *et al.*, 2000; Ohkushi *et al.*, 2005). Furthermore, extremely depleted carbon isotopic values of benthic foraminiferal tests may be related to calcite overgrowths on foraminiferal tests that exhibit an unusual brown color (Ohkushi *et al.*, 2005). In this case, methane hydrate dissociation was suggested as a possible cause of depleted carbon isotopic values in forminiferal tests. Strongly depleted ^{13}C values for foraminiferal test from nearby localities may support that the seeping of methane gas was derived from the dissociation of hydrate (Nam and Lee, 2009). Related research from the Japan Sea/East Sea clearly showed gas hydrate dissociation through the upward flux of biogenic methane, based on experiments on gas and pore-water composition (Bahk *et al.*, 2009). Similarly, abundant carbonate nodules scattered throughout sediment from nearby coring sites may support the interpretation of gas hydrate seepage, caused by hydrate dissociation (Yoo *et al.*, 2008). Therefore, the highly depleted carbon isotopic values from core 06GHSA P6 likely may support methane hydrate dissociation.

Methane hydrate dissociation and paleoceanographic implications

Methane hydrate forms where thermodynamic conditions permit and where methane concentrations in water exceed a threshold level, but becomes concentrated only in areas where gas movement is focused (Clennell *et al.*, 2003). Hydrate formation results in the removal of water and methane from the sediment pore space. The formation and decomposition of methane hydrate is believed to exert a strong influence on the mechanical properties of marine sediment (Max, 2003). Until recently, however, the conditions under which methane hydrate forms, accumulates, migrates, and dissociates remain poorly understood (Clennell *et al.*, 2003).

In general, methane hydrate dissociation occurs when the gas hydrate stability field (GHSF) collapses of which there are several possible causes. One triggering mechanism is pressure change. Kennett *et al.* (2000) examined both planktonic and benthic foraminiferal carbon isotope variations in sediments from the Santa Barbara Basin, and concluded that extremely light carbon and oxygen isotopic signals in specific layers strongly correlated with known periods of temperature change during global interstadials. These extremely light carbon isotopic values were explained as the result of episodic hydrate dissociation and methane seepage during intervals of warm-water intrusion, which resulted from decrease in pressure during interstadial periods. Co-variation of depleted carbon isotope values from foraminifera and ice-core methane contents from the GISP2 have been documented in sediments from the low-latitude Gulf of Papua (Garidel-Thoron *et al.*, 2004). Also, methane release from methane hydrate reservoirs in the continental margin of the northwestern Pacific Ocean showed that both planktonic and benthic foraminifera have highly depleted carbon isotope values. In their study, most foraminiferal tests were brown, as a result of post-depositional alteration, and yielded highly negative carbon isotopic values (Ohkushi *et al.*, 2005). Similarly, episodic methane release was in-

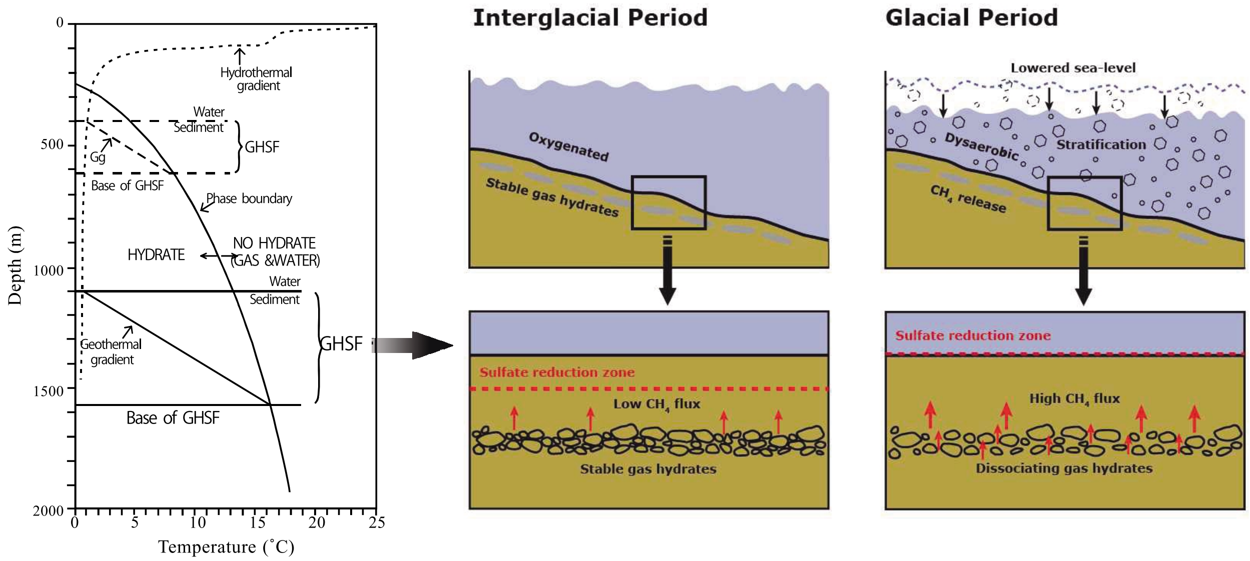

Fig. 6. An illustration of gas hydrate stability field (GHSF) in the Japan Sea/East Sea (left figure, modified from Ryu et al. (1999)). Schematic model for methane hydrate dissociation in the Japan Sea/East Sea resulting from lowered sea levels (right figure). Shoaling of sea levels and sulfate reduction zones during glacial periods directly influence the dissociation of gas hydrate.

terpreted as a consequence of pressure changes, intermediate water influx, as well as the lowering of sea level (Uchida *et al.*, 2004), possibly associated with events such as plate-boundary earthquakes near the coring site (Ohkushi *et al.*, 2005).

Another potential possibility of the methane emission is due to the collapse of a methane hydrate stability field. Previous research has shown that sea levels have fluctuated between glacial and interglacial periods by as much as 130 m (Fairbanks, 1989) and that the present-day sea level around the Korean Peninsula was established approximately 6~7 ka ago. An important factor of influence on paleoenvironmental changes of the Japan Sea/East Sea is the change in sea-water ventilation that should be controlled directly by sea-level changes. Intrusion or demise of the Warm Tsushima Current (WTC) contributed to environmental changes and intrusion of cold intermediate water from the Tsugaru Strait during glacial and transitional periods may affect the formation of intermediate water in the Japan Sea/East Sea (Ahagon *et al.*, 2003). There is evidence for the intrusion of intermediate water through the Tsugaru Strait during glacial periods, and therefore, cold and warm water coexisted in the Japan Sea/East Sea during glacial intervals (Takei *et al.*, 2002). This evidence also supports the idea that sea-level changes may have triggered gas hydrate destabilization.

Laboratory experiments suggest the presence of a gas hydrate stability zone (GHSF) in the Japan Sea/East Sea (Ryu *et al.*, 1999). The lower boundary of the GHSF would be approximately 210 m beneath a sea-floor at a depth of 400 m, and about 480 m below a sea-floor at a depth of 1,100 m. Such boundary positions are compatible with the position of the bottom simulated reflector (BSR) obtained from seismic data. The water depth of the core localities in this study is 1189 m (for the core 06GHSA P6), and it is close to the modeled position of the GHSF (Fig. 6). Slight changes in pressure resulting from sea-level changes may affect the GHSF, as depicted in a model based on experimental results (Fig. 6). A similar mechanism of sea-level change was suggested by Hiruta *et al.* (2009) for the Joetsu Basin, on the eastern margin of the Japan Sea/East Sea, in which methane hydrate preserved in deep sediments was under a stable GHSF during interglacial periods, but the pressure decrease caused by falling sea-levels during glaciation caused destabilization of the GHSF.

Several studies have examined slope failure as a mechanism for hydrate dissociation (e.g., Paull *et al.*, 2003). The southern part of the Ulleung Basin is characterized by gentle slopes that steepen toward the center of the basin. Steeper slopes can foster unstable slope conditions, particularly when sea levels were lower during glacial intervals. Geophysical and seismic studies have identified numerous lobe structures in the southern part of the Ulleung Basin, which are believed to be debris flow deposits caused by slope failure (Lee *et al.*, 1999). Sudden slope collapse affects gas hydrate stability, therefore, this evidence of slope failure in the southern Ulleung Basin, Japan Sea/East Sea points to the possibility that methane hydrate was dissociated during glacial intervals.

During stable GHSF intervals, the source of diploptene would have been predominantly cyanobacteria. When the GHSF was unstable during glacial episodes, however, much of the diploptene may have been produced by methanotrophic bacteria. The strongly depleted carbon isotopic values of diploptene during glacial periods suggest that the diploptene source during glacial versus interglacial intervals varied, and favors an explanation in which methane hydrate dissociation is accompanied by the synthesis of diploptene by methanotrophic bacteria. Carbonate nodules, which are commonly present in methane-seep environments (Pape *et al*., 2005) and related to the dissociation of gas hydrate (Chen *et al*., 2007), have been reported from other locations, and authigenic carbonates were reported in sediments from the sites nearby (Yoo *et al*., 2008; Bahk *et al*., 2009), both of which support the concept of methane hydrate dissociation during glacial episodes.

CONCLUSION

Geochemical investigations of two piston cores (06GHSA P1, 06GHSA P6) from the Ulleung Basin of the Japan Sea/East Sea provide a clear differentiation in deploptene content and its carbon isotope values between glacial and interglacial periods. In particular, high concentration of deploptene (~600 ng/g) and their strongly depleted carbon isotope values (~–61.3‰) suggest strong methanotrophic bacterial activity during glacial periods. Further, this implies that methane hydrate dissociation results in strongly depleted carbon isotopes during glacial periods, whereas heavier carbon isotopic value occurred during Holocene in both cores could be derived from cyanobacterial activities. One of the plausible and inferred mechanisms for hydrate dissociation during glacial episodes is closely related to lowered sea levels (collapse of hydrate stability zone), thus paleoceanographic and hydrate instability, although slope failure also remains as another possible mechanism.

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