Quaternary Research 80 (2013) 606–613

Contents lists available at ScienceDirect

Quaternary Research

journal homepage: www.elsevier.com/locate/yqres

Mercury content as a new indicator of ocean stratification and primary productivity in Quaternary sediments off Bahama Bank in the Caribbean Sea

Itsuro Kita [a,*], Makoto Kojima [a], Hidenao Hasegawa [b], Shun Chiyonobu [c], Tokiyuki Sato [d]

[a] Department of Environmental Changes, Faculty of Social and Cultural Studies, Kyushu University, Fukuoka 819-0395, Japan
[b] Institute for Environmental Sciences, Aomori 039-3212, Japan
[c] Research Institute of Innovative Technology for the Earth, Kyoto 619-0232, Japan
[d] Faculty of Engineering and Resource Science, Akita University, Akita 010-8502, Japan

ARTICLE INFO

Article history:
Received 12 December 2012
Available online 8 October 2013

Keywords:
Mercury
Nannoplankton assemblages
Nitrogen and carbon isotopes
Quaternary marine sediment
Ocean stratification
Primary productivity
Climatic change
Caribbean Sea

ABSTRACT

We report the first evidence of Hg content in marine sediments changing in connection with the climate-driven changes in ocean stratification during the Quaternary Period based on core samples from ODP Hole 1006A off Great Bahama Bank in the Caribbean Sea. The Hg content ranged from 5.9 to 60.7 ng/g with an average value of 33.1 ng/g during 350 and 1330 ka and changed inversely with $\delta^{18}O_{planktonic}$ values. The change in Hg content was positively correlated with total organic carbon (TOC) content, indicating connections between the $\delta^{15}N_{org}$ and $\delta^{13}C_{org}$ values of organic matter and the absolute abundance of a deep-dwelling calcareous nannoplankton (*Florisphaera profunda*). The marine Hg is thought to have been incorporated into the organic matter produced by deep-dwelling phytoplankton. Based on these results, we propose a mechanism by which marine Hg can collect in a thermocline formed in the stratified lower photic zone. Mercury content and nannoplankton assemblage in marine sediment provide information about the extent of stratification of the oceanic photic zone and the role of surface- and deep-dwelling phytoplankton in producing marine organic matter and changing its $\delta^{15}N_{org}$ and $\delta^{13}C_{org}$ values.

Introduction

Mercury increasingly concentrates up the food chain from plankton to fishes, other marine animals and humans (Nishigaki and Harada, 1975; Leah et al., 1991; Nakagawa et al., 1997; Al-Majed and Preston, 2000). Concentrated Hg, especially methylated Hg, is responsible for the famous Minamata disease (Nishigaki and Harada, 1975; Kudo et al., 2000). However, methylated Hg represents only a small percent of the total Hg concentration in ocean water and does not significantly affect the overall distribution of Hg in the oceans (Laurier et al., 2004).

The depth profiles of Hg content in the Pacific and Atlantic Oceans have been reported since the 1980s (Gill and Fitzgerald, 1987, 1988; Mason et al., 1995; Mason and Sullivan, 1999; Laurier et al., 2004). Gill and Fitzgerald (1987) reported that surface seawater Hg measurements in the central Pacific Ocean along 160°W from 20°N to 20°S exhibited a 60% decrease in Hg in the equatorial upwelling area. This drop in Hg was thought to be caused by phytoplankton consuming Hg in the photic zone which has high total concentrations of nitrate and nitrite. Furthermore, Gill and Fitzgerald (1988) and Laurier et al. (2004) reported different depth profiles of Hg content in photic water in several areas and mentioned that these depth profiles can be caused by the addition of rain or land water or external sources. Therefore, the Hg in photic water mainly originates from wet and dry deposition. Mercury dissolved in rain water and adsorbed on dry particles is distributed globally by atmospheric circulation and reaches polar areas (e.g., Vandal et al., 1993; Iverfeldt et al., 1995; Olmez et al., 1998). Vandal et al. (1993) reported that Hg flux to Antarctica over the past 34,000 yr increased during the last glacial maximum, showing that it is climatically controlled.

Changes in Hg content in the photic zone at different depths may be related to the consumption by phytoplankton, which deposits Hg-bearing sediment on the sea floor. However, evidence of a relationship between sediment Hg content and phytoplankton absolute abundance has not been previously reported. In addition, Laurier et al. (2004) describe seasonal changes in Hg in the surface photic water caused by the annual development of a near-surface seasonal thermocline. Glacial–interglacial variability of Hg in the photic water must be greater than the seasonal variability in the present photic zone. Therefore, it is likely that phytoplankton consumes the Hg accumulated in the stratified photic zone, depositing more Hg–bearing sediment on the sea floor than phytoplankton from the stirred photic zone. Thus, the climatically controlled variations of Hg in the photic zone may be recorded

---

* Corresponding author.
E-mail address: kita@scs.kyushu-u.ac.jp (I. Kita).

0033-5894/$ – see front matter © 2013 University of Washington. Published by Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.yqres.2013.08.006

in the sediments, and sediment Hg may be used as a chemical indicator of photic zone stratification and its collapse.

Mercury contents of recent widely distributed marine sediments show a wide range of <10–2000 ppb with mean value of 100 ppb (Jonasson and Boyle, 1972). In the North Atlantic Ocean and Eastern Mediterranean Sea, Mercone et al. (1999) reported Hg concentrations varying from 20 to 500 ppb in turbidite and sapropel layers with high TOC contents deposited at depths less than 2 m.

In Quaternary marine sediments lacking such external sources, however, the long-term fluctuations of Hg content have not been previously reported. Because phytoplankton can be attributed to marine Hg concentrations, phytoplankton likely contributes to Hg accumulation in Quaternary marine sediments, even though the concentration is lower than approximately 2 pM (e.g., Gill and Fitzgerald, 1987; Laurier et al., 2004).

The phytoplankton in marine environments is controlled by nutrient content in the photic zone. The depth profile of its content can be changed by the mixing of oligotrophic photic water with the eutrophic deeper water (Kroopnick, 1985; Liu and Kaplan, 1989). The mixing of these two waters can be driven by winds; changes in mixing strength are closely linked to wind strength and climate change. In monsoon and trade-wind areas, the ascent of deeper water into the photic zone is known as upwelling. When winds are weaker, the photic zone becomes stratified.

Calcareous nannoplankton (coccolithophores) are a major component of oceanic phytoplankton and have been used to interpret paleoclimate and paleoenvironment (e.g., Haq, 1980; Sato and Kameo, 1996; Bollmann, 1997; Sato et al., 2004). Furthermore, calcareous nannoplankton include both surface- and deep-dwelling species. *Florisphaera profunda* (*F. profunda*) is a deep-dwelling species of calcareous nannoplankton (Okada and Honjo, 1973; Molfino and McIntyre, 1990; Beaufort, 1996; Beaufort et al., 1997; Chiyonobu et al., 2006). Based on core samples from the Indian Ocean, Beaufort et al. (1997) suggested that the abundance of *F. profunda* in fossil assemblages can be used to monitor the depth of the nutricline in paleoproductivity studies because the relative abundance of this species increases when the upper photic zone is nutrient poor and the nutricline is deep. Chiyonobu et al. (2006) used the absolute abundance of *F. profunda* to evaluate the extent of stratification of the photic zone off Peru in the equatorial Pacific Ocean. In addition, Beaufort (1996) reported that the percentage of *F. profunda* was inversely related to organic carbon content in sediments from the equatorial Indian Ocean over the last 260,000 yr and concluded that coccolithophorids are excellent indicators of variations in ocean productivity. Therefore, the change in nannoplankton assemblages may be used to identify which surface- and deep-dwelling phytoplankton species are responsible for the changes in productivity of organic matter and its nitrogen and carbon isotopic ratios ($\delta^{15}N_{org}$ and $\delta^{13}C_{org}$) which are controlled by the consumption of nitrate and total carbonic acid (ΣCO_2) (Hayes, 1993; Nakatsuka et al., 1995; Kita et al., 2009). However, direct comparisons between changes in these biological and chemical data in relation to Hg content have seldom been described in connection with photic zone stratification and collapse.

In this study, we used core samples from ODP Hole 1006A off Great Bahama Bank in the Caribbean Sea during a period from 350 to 1330 ka, because Hasegawa et al. (2003) and Kita et al. (2009) have observed that organic matter $\delta^{15}N_{org}$ values change with the absolute abundance of surface-dwelling nannoplankton species, indicating a positive correlation with 100,000- and 41,000-yr variations in $\delta^{18}O_{planktonic}$ values of planktonic foraminifera (*Globigerinoides ruber* (d'Orbigny 1839)). Most of the core samples are composed of nannofossil ooze. By using this core, we assume that the activities of surface- and deep-dwelling nannoplankton species are representative of other phytoplankton occurring in the upper and lower photic zones. The primary goal of this study is to show evidence that changes in Hg content in marine sediments were caused by climatic change of phytoplankton activity and may be used as a chemical indicator of photic zone stratification and collapse. The role of surface- and deep-dwelling phytoplankton in producing Hg-bearing organic matter and changing its $\delta^{15}N_{org}$ and $\delta^{13}C_{org}$ values was discussed using calcareous nannoplankton as a representative of phytoplankton.

Location of ODP Hole 1006A, its geological setting, and sedimentary ages of core samples

ODP Hole 1006A (24°24′N, 79°28′W) was drilled 717.3 m below the sea floor (mbsf) at a depth of 658 m off Great Bahama Bank in the Caribbean Sea (Shipboard Scientific Party, 1997) (Fig. 1). Sediment core samples from 13.7 to 55.2 mbsf were used in this study. Almost all of the samples are nannofossil ooze with foraminifera and a small amount of needlelike aragonite in the absence of layers with high TOC content, such as turbidite and sapropel. Microfossils are well preserved. The number of shallow benthic foraminifera reworked from neritic environments is less than 10% of their total number (Shipboard Scientific Party, 1997) suggesting weak contamination of terrestrial matter to the sediment in this hole. Sedimentary ages (350–1330 ka) of core samples used in this study were determined by Kroon et al. (2000) based on the $\delta^{18}O_{planktonic}$ value of planktonic foraminifera (*G. ruber* (d'Orbigny)), magnetostratigraphy and U–Th age determination (Shipboard Scientific Party, 1997; Henderson et al., 2000). Reference points of age determination using calcareous nannofossils include the first occurrence of *Emiliania huxleyi* (Lohmann) Hay and Mohler and large *Gephyrocapsa* spp. and the last occurrence of *Pseudoemiliania lacunosa* (Kamptner) Gartner, *Reticulofenestra asanoi* Sato and Takayama, and large *Gephyrocapsa* spp. (Sato and Kameo, 1996).

Methods

Measurement of mercury content in sediments

Samples (86) were collected at approximately 50-cm intervals. A powdered core sample (approximately 10–20 mg) was covered with two reagents (activated alumina and a mixture of Na_2CO_3 and NaOH, referred to here as B and M, respectively (Nippon Instruments Co.)) on a ceramic board inserted into the equipment with a heating system (Mercury Atomizer MA-1S, Nippon Instruments Co.). The sample was burned for 10 min at 750°C, and the released Hg was trapped as a gold amalgam after it passed through a trap with a buffer solution of pH 7 by using Hg-free air as a carrier gas. Subsequently, the Hg vapor stripped from the amalgam by the heat was introduced into Mercury detector/D-2 (Nippon Instruments Co.) using flameless atomic absorption. The amount of Hg was measured within an error of 2%, resulting in maximum errors of 8 and 5% for Hg amounts less than 10 and 20 ng/g, respectively. The reagents (B and M) and buffer solution were used to purify the Hg of gases, such as CO_2 and SO_2, released by the combustion of sediment samples.

Absolute abundance of calcareous nannoplankton in core samples

To measure the absolute abundance of calcareous nannoplankton, a powdered sample of 0.040 g was dispersed in 50 ml of water. A portion (0.5 ml) of the solution was then dried and hardened on the cover glass using ultraviolet light. The number of nannoplankton in an 18 mm × 20 μm area was counted through a 1500× microscope and converted into an amount contained in 1 g (specimens/g). This procedure is described in detail in Chiyonobu et al. (2006).

Total organic carbon and nitrogen contents and their isotopic ratios

Sediment samples of 0.5 to 1.0 g weight were dissolved by HCl (1 N) to remove carbonate. The residue (10–30 mg) was wrapped in tin foil and put into an elemental analyzer (ThermoQuest, NC2500) to measure