Available online at www.sciencedirect.com
ScienceDirect
Deep-Sea Research I 54 (2007) 1571–1592
DEEP-SEA RESEARCH PART I
www.elsevier.com/locate/dsri

Seasonal and depth variations in molecular and isotopic alkenone composition of sinking particles from the western North Pacific

Masanobu Yamamoto[a,*], Akifumi Shimamoto[b], Tatsuo Fukuhara[b], Hiroshi Naraoka[c], Yuichiro Tanaka[d], Akira Nishimura[d]

[a]*Faculty of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan*
[b]*The General Environmental Technos Co., LTD., Osaka 541-0052, Japan*
[c]*Department of Earth Sciences, Okayama University, Okayama 700-8530, Japan*
[d]*National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8567, Japan*

Received 30 August 2006; received in revised form 18 May 2007; accepted 24 May 2007
Available online 7 June 2007

Abstract

Seasonal and depth variations in alkenone flux and molecular and isotopic composition of sinking particles were examined using a 21-month time-series sediment trap experiment at a mooring station WCT-2 (39°N, 147°E) in the mid-latitude NW Pacific to assess the influences of seasonality, production depth, and degradation in the water column on the alkenone unsaturation index $U_{37}^{K'}$. Analysis of the underlying sediments was also conducted to evaluate the effects of alkenone degradation at the water–sediment interface on $U_{37}^{K'}$. Alkenone sinking flux and $U_{37}^{K'}$-based temperature showed strong seasonal variability. Alkenone fluxes were higher from spring to fall than they were from fall to spring. During periods of high alkenone flux, the $U_{37}^{K'}$-based temperatures were lower than the contemporary sea-surface temperatures (SSTs), suggesting alkenone production in a well-developed thermocline (shallower than 30 m). During low alkenone flux periods, the $U_{37}^{K'}$-based temperatures were nearly constant and were higher than the contemporary SSTs. The nearly constant carbon isotopic ratios of $C_{37:2}$ and $C_{38:2}$ alkenones suggest that alkenones produced in early fall were suspended in the surface water until sinking. The alkenone sinking flux decreased exponentially with increasing depth. The decreasing trend was enhanced during the periods of high alkenone flux, suggesting that fresh and labile particles sank from spring to fall, while old and stable particles sank from fall to spring. The $U_{37}^{K'}$-based temperature usually increased with increasing depth. The preservation efficiency of alkenones was ~2.7–5.2% at the water–sediment interface. Despite the significant degradation of the alkenones, there was little difference in $U_{37}^{K'}$ levels between sinking particles and the surface sediment.

Keywords: Alkenones; Unsaturation index; Sediment trap; The North Pacific; Carbon isotopes

1. Introduction

Long-chain alkenones are biolipids in a specific group of haptophyte algae (Volkman et al., 1980), and, until now, they have been reported solely from *Emiliania* and *Gephyrocapsa* (Family Gephyrocapsae)

*Corresponding author. Tel.: +81 11 706 2379; fax: +81 11 706 4867.
E-mail address: myama@ees.hokudai.ac.jp (M. Yamamoto).

0967-0637/$ - see front matter
doi:10.1016/j.dsr.2007.05.012

and *Chrysotila* and *Isochrysis* (Family Isochrysidaceae) (Marlowe et al., 1984; Volkman et al., 1995). In open marine environments, alkenones are thought to be produced exclusively by *Emiliania* and *Gephyrocapsa* (Marlowe et al., 1984, 1990).

Alkenone paleothermometry was proposed in the mid-1980s (Brassell et al., 1986; Prahl and Wakeham, 1987) and has been widely applied to the assessment of late Quaternary changes in sea-surface temperatures (SSTs) (reviewed by Brassell, 1993; Müller et al., 1998). Alkenone paleothermometry uses the physiological response of the unsaturation degree of C_{37} alkenones (expressed as U^{K}_{37} and $U^{K'}_{37}$) to the growth temperature. An early attempt exhibited a linear relationship between alkenone unsaturation indices and growth temperature in a batch culture experiment with an *Emiliania huxleyi* strain (55a) from the NE Pacific (Prahl and Wakeham, 1987; Prahl et al., 1988). Nearly identical relationships were found in a comparison of the $U^{K'}_{37}$ of core-top and surface sediments with the mean annual temperature at 0 m in the overlying waters (e.g., Müller et al., 1998; Conte et al., 2006). The calibration equations based on these relationships have been used for assessing sea-surface paleotemperature. Recently, Conte et al. (2006) showed that the surface sediment calibration differs significantly from the surface-water calibration and attributed the deviation to the combined effects of seasonality and thermocline production as well as the differential degradation of tri- and di-unsaturated alkenones.

The season and depth of alkenone production determine the value of sedimentary $U^{K'}_{37}$. It is thus necessary to evaluate the effects of these factors on paleotemperature estimation. Because the alkenones sampled by time-series sediment traps record the temperature when and where the alkenones were produced, the temperatures indicated by trapped alkenones provide a key for estimating the season and depth of alkenone production. In the northwestern Pacific, Sawada et al. (1998) reported that the $U^{K'}_{37}$-based temperatures in sinking particles corresponded with the SSTs 1–2 months prior to sampling at the southern margin of the Kuroshio–Oyashio mixing zone. Ohkouchi et al. (1999) argued that alkenones record the temperatures within or below the thermocline (~150 m deep) because the alkenone temperatures in surface sediments were nearly 10 °C lower than annual mean SSTs in the overlying water in the subtropical Pacific. In the subarctic Pacific, Harada et al. (2006) reported that $U^{K'}_{37}$-based temperatures in sinking particles corresponded with the thermocline temperatures during the high-export season, while they were higher than SSTs during the low-export season.

Degradation of alkenones through water and sediment columns presumably affects the alkenone unsaturation index (Freeman and Wakeham, 1992; Hoefs et al., 1998; Gong and Hollander, 1999). If this effect is relatively large, it introduces error into paleotemperature estimations that are based on the alkenone unsaturation index. Alkenone degradation through the water column is evaluated based on the decreasing trend of sinking flux with increasing depth (Müller and Fischer, 2001). Most sediment trap studies, however, have not detected this decreasing trend because of interference by the lateral influx of allochthonous alkenones to deeper traps (e.g., Sawada et al., 1998). Also, very little is known about the degradation rate of alkenones at the water–sediment interface, except for a few studies (e.g., Prahl et al., 1993; Müller and Fischer, 2001). Evaluation requires a combined data set of the sinking fluxes of alkenones through the water column and their accumulation rates in the sediment at the same location.

Lateral advection of allochthonous alkenones by strong surface currents can also alter the alkenone signal. High $U^{K'}_{37}$-based temperature in the southern Indian Ocean during the last Glacial maximum has been interpreted as the lateral advection of warm-water detrital alkenones by the Agulhas Current (Sicre et al., 2005). Other research has attributed the low $U^{K'}_{37}$-based temperature of the suspended particulates in the Brazil–Malvinas Confluence to the lateral advection of cold-water detrital alkenones by the Malvinas Current (Rühlemann and Butzin, 2006; Conte et al., 2006).

In this study, we examined the seasonal and depth variations in alkenone flux and molecular and isotopic compositions of sinking particles using a time-series sediment trap experiment at a selected mooring station (39°N, 147°E; Fig. 1) in the mid-latitude NW Pacific to assess the influences of seasonality, production depth, and degradation of alkenones in the water column on $U^{K'}_{37}$. Analysis of the underlying sediments was also conducted to evaluate the effects of alkenone degradation at the water–sediment interface on $U^{K'}_{37}$.

The study site, station WCT-2, is located in the mixing zone between Oyashio and Kuroshio waters (Fig. 1). Cold and warm mesoscale eddies from the Oyashio and Kuroshio, respectively, develop in the