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Alkenones as tracers of surface ocean temperature and biological pump processes on the Northwest Atlantic margin

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ABSTRACT

We have examined alkenone distributions, specifically the temperature proxy $U^{K'}_{37}$, in sinking particulate organic matter (POM) intercepted at three depths by time-series sediment traps deployed between 2004 and 2007 on the Northwest Atlantic margin. The goal was to assess physical and biogeochemical processes acting upon alkenones during passage through the water column. $U^{K'}_{37}$ did not exhibit any systematic trend with increasing depth despite several-fold attenuation in alkenone flux. Because of the extensive reduction in C_{37} alkenone flux in the water column and more efficient alkenone degradation during the period of high alkenone flux, the temperature bias toward that of more productive seasons was reduced with increasing trap depth. The temporal variation of $U^{K'}_{37}$ and alkenone-derived temperature compared best with the satellite-derived SST at an upstream region approximately 160 km east of the mooring site with a time lag of about 30 days, suggesting this region as the dominant source of alkenone-bearing POM. The alkenone-derived temperature of core-top sediments (15 °C) at the study site was lower than the flux-weighted average alkenone-derived temperature of sinking POM at 50 m above the seafloor. This discrepancy may reflect additional supply of resuspended sediment carrying alkenones produced in cooler waters to the northeast, and transported in bottom nepheloid layers.

1. Introduction

Since the first discovery of the relationship between alkenone unsaturation and the temperature of water where the organisms grow (Brassell et al., 1986; Prahl and Wakeham, 1987), the alkenone unsaturation index ($U^{K'}_{37}$) proxy, defined as a ratio of di-unsaturated C_{37} methyl ketone ($[C_{37:2}]$) to the sum of di- and tri-unsaturated C_{37} methyl ketones ($[C_{37:2}+C_{37:3}]$), has been widely used in paleoceanographic reconstructions (for example, Sachs et al., 2000; Herbert, 2003). One persistent question is why $U^{K'}_{37}$ of surface sediment is correlated strongly with mean annual sea surface temperature (SST) despite strong seasonal variations in alkenone production and export flux that could potentially bias the temperature towards periods of maximum growth. This temperature bias may thus be more severe over continental margins where rapid transit to sediment and high sedimentation rates may not provide enough time for remineralization of the pulse of sinking particulate organic matter (POM). However, this process has yet to be confirmed by field studies.

A related issue is whether $U^{K'}_{37}$ is altered by various biotic and abiotic degradation during passage through the water column and subsequent burial (see a recent review of Rontani et al., 2013 and references therein). Tiered sediment trap arrays are useful tools for answering these questions since they facilitate examination of how alkenones signals (e.g., $U^{K'}_{37}$ values) are transferred from surface waters to depth (for example, Rosell-Melé and Prahl, 2013).

In addition to the application of $U^{K'}_{37}$-derived temperature (hereafter $T_{alkenone}$) for reconstruction of past ocean conditions, alkenones can provide insights into the oceanic processes that influence POM cycling. In particular, because these compounds are exclusively synthesized by a specific class of marine phytoplankton, they serve as excellent tracers of alkenone-bearing POM derived from surface ocean productivity. One example is the use of these compounds to reveal an important role for lateral transport in the dispersal of POM by ocean currents, especially on the continental margins (Benthien and Müller, 2000; Mollenhauer et al., 2006; Ruhlemann and Butzin, 2006; Hwang et al., 2009a; Kusch et al., 2010). $U^{K'}_{37}$ measurements

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combined with radiocarbon analysis of alkenones have revealed long-range transport of organic matter associated with resuspended sediments (Ohkouchi et al., 2002). By comparison of temporal variations in $T_{alkenone}$ of sinking POM intercepted at depth with that of SST, insights on the processes such as packaging and export of POM, and sinking speed of particles may be gained (Knappertsbusch and Brummer, 1995; Müller and Fischer, 2001; Conte et al., 2003). Temperate oceans, with large seasonal variations in SST are especially appropriate for this application due to high-amplitude variations in $T_{alkenone}$ that can be tracked through the water column.

A recent time-series biogeochemical flux study was established to examine POM cycling on the NW Atlantic margin (Hwang et al., 2009a). This region of the New England slope has been the subject of a sustained physical oceanographic observation program designed to explore the variability of the Deep Western Boundary Current (DWBC), a deep limb of the Atlantic meridional overturning circulation, and the Gulf Stream system (Joyce et al., 2005; Toole et al., 2011). A particular focus of this time-series study was an assessment of the influence of the DWBC and associated lateral particle transport on the biogeochemical properties of sinking and suspended particles and bottom sediments along the path of this undercurrent (Hwang et al., 2009a, 2009b). Radiocarbon measurements in association with other biogeochemical data such as aluminum concentrations and long-chain saturated fatty acid concentrations indicated that supply of laterally transported resuspended sediment contributed considerably to sinking and suspended POM at the study site (Hwang et al., 2009a, 2009b). As a part of this time-series biogeochemical flux study, we utilize $U^{K'}_{37}$ data as a window into POM cycling over this highly productive continental margin. We also take advantage of the $U^{K'}_{37}$ data of sinking POM to provide insights into some of the unresolved questions mentioned above concerning the transfer of molecular proxy signals emanating from surface waters to depth.

2. Methods

Various types of samples were collected on the NW Atlantic margin from 2004 to 2007.

Three conical sediment traps (McLane Mark-7, Honjo and Doherty, 1988) were deployed at three nominal depths – 1000 m, 2000 m, and 3000 m (~50 m above the bottom) – on a single bottom-tethered mooring on the NW Atlantic margin (39°28′N, 68°22′W; Fig. 1; see Table 1 for details of trap depths, bottom depths, and sampling intervals for the three deployments). Sinking particles were collected from June 27, 2004 to April 27, 2005, from July 1, 2005 to June 1, 2006, and from June 27, 2006 to June 1, 2007. About 5 g/L of sodium chloride was added to seawater that was used to fill the collection cups. For 2004–5, and 2005–6 deployments, collection cups of the 1000 m and 2000 m traps were filled with seawater treated with various preservatives such as $HgCl_2$, formalin, Lugol's solution, DMSO (dimethyl sulfoxide), and HISTOCHOICE™ for the purpose of testing their relative efficiency for DNA preservation (Dennett and Manganini, 2006; not discussed further in this paper). Collection cups for the other samples were filled with seawater treated with $HgCl_2$ (0.3% by wt). Samples were stored at 4 °C until subsampling and further analyses. Each sieved sample (< 1 mm) was divided into ten equal aliquots using a wet sample splitter (WSD-10, McLane Research Laboratories, Inc.) and used for biogeochemical analyses.

Surface water suspended particles were collected by filtration of water from the ship's uncontaminated seawater intake (nominal sampling depth = 2.4 m) using 293 mm diameter filters (Gelman Science, type A/E glass fiber) for several hours per sample (Hwang et al., 2009b) during cruises aboard the R/V *Endeavor* in June 25–July 2, 2005 and the R/V *Oceanus* in June 22–27, 2006 (Table 2).

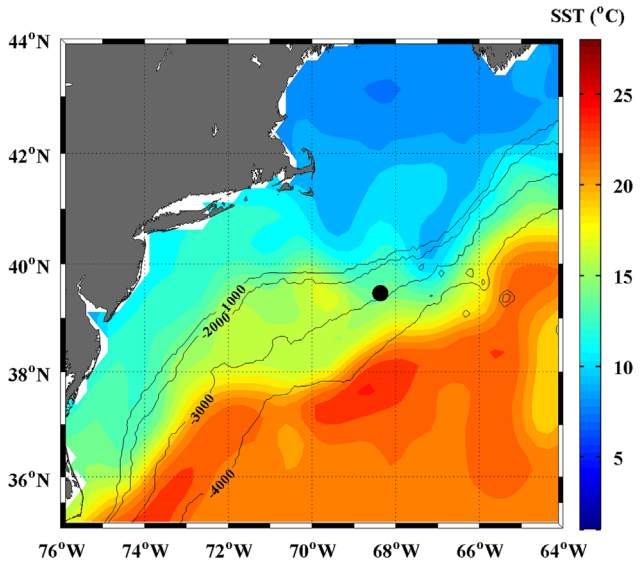

Fig. 1. Satellite-derived sea surface temperature (SST) on January 1, 2005 overlapped with bathymetry in the northwest Atlantic. Sediment trap mooring station is indicated.

Because the water was not pre-filtered using a large-mesh screen, the surface POM samples also include plankton. Each filter was folded and stored frozen at –20 °C in a pre-combusted aluminum foil pouch until analysis.

One tenth splits of each sediment trap sample, equivalent to ~30 to 4000 mg dry weight, were freeze-dried and used for determination of $U^{K'}_{37}$. Total lipid extracts were extracted into a mixture of methylene chloride and methanol (93:7 by volume) using an accelerated solvent extraction system (DIONEX ASE 200). Sample #9 of the 1000 m trap, 21 samples of the 2000 m trap, and samples #4, 6,8, 10, 12,14, 16, 18, 20 of the 3000 m trap from the 2006–7 deployment were extracted using a microwave accelerated reaction system (MARS, CEM Corporation) (these samples are indicated as half-filled symbols in Fig. 2). Although this has not been rigorously tested, we suspect that MARS has a greater extraction efficiency than ASE (Valier Galy, personal communication), as the saw-tooth concentration pattern observed for the 3000 m trap samples of the 2006–7 periods appears suspicious. However, this saw-tooth pattern was also observed for the 2000 m trap every sample of which was extracted using MARS. We have not found any suspicious pattern in $U^{K'}_{37}$ for the corresponding samples. This uncertainty does not affect our interpretation because the majority of the samples were extracted with the ASE system and hence the results maintain consistency. Also, our discussion on alkenone concentration and flux is focused on comparison among our own samples collected at different depths rather than comparison with other reported data.

Details of treatment of lipid samples for alkenone analysis have been published elsewhere (Hwang et al., 2009b). Alkenone concentrations and distributions were determined using an HP-5890II gas chromatograph/flame ionization detector (GC/FID) equipped with a capillary column (Varian, CP-SIL 5CB, 0.25 mm ID × 0.25 μm film thickness, either 60 m or 30 m in length) at Woods Hole Oceanographic Institution. 21 samples of the 2000 m trap from the 2006–7 deployment were analyzed using an Agilent 7890A GC/FID at ETH, Zürich. Alkenones were quantified by comparison to a C_{36} *n*-alkane external standard added immediately before injection to GC. Usually peaks of C_{37} alkenones are resolved well by baseline separation. However, for the samples #12 of the 1000 m trap and #19 of the 3000 m trap of 2006–7 deployment, the peaks of $C_{37:2}$ and $C_{37:3}$ were broad and incompletely separated resulting in erroneous peak area determination and consequently, no $U^{K'}_{37}$