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Further insights into how sediment redox status controls the preservation and composition of sedimentary biomarkers

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ABSTRACT

Sedimentary biomarker distributions can record ocean productivity and community structure, but their interpretation must consider alteration during organic matter (OM) export and burial. Large changes in the water column redox state are known to impact on the preservation of biomarkers, but more subtle variation in sediment redox conditions, characteristic of major modern ocean basins, have been less thoroughly investigated. Here we evaluate changes in biomarker distributions during sinking and burial across a nearshore to offshore transect in the southwestern Cape Basin (South East Atlantic), which includes a range of sedimentary environments. Biomarker concentrations and distributions in suspended particulate matter from the upper water column were determined and compared with underlying sedimentary biomarker accumulation rates and distributions. Biomarker distributions were similar in surface and subsurface waters, indicating that the OM signature is exported from the ocean mixed layer with minimal alteration. We show that, while export production (100 m) is similar along this transect, $^{230}Th_{xs}$-corrected biomarker accumulation rate varies by over an order of magnitude in sediments and is directly associated with sedimentary redox conditions, ranging from oxic to nitrogenous–ferruginous. Biomarker distributions were dominated by sterols in surface water, and by alkenones in underlying sediments, which we propose to be primarily the result of selective preservation. Notably, the difference in sediment O_2 penetration depth was associated with relative biomarker preservation. Subtle variation in sedimentary redox conditions has a dramatic impact on the distribution of preserved biomarkers. We discuss mechanisms for preferential degradation of specific biomarkers within this setting.

1. Introduction

The use of sedimentary biomarker concentrations to reconstruct palaeoceanographic changes has increased in the last 20 yr (e.g. Grimalt et al., 2000; Sicre et al., 2000; Werne et al., 2000). Most studies reconstructing palaeoproductivity variation have focussed on alkenones, sourced from well constrained reticulofenistrid haptophytes such as *Emiliania huxleyi* (Volkman et al., 1980). Other studies have, however, used proportional abundances or distributions of sterols, alkenones and/or phytol to infer changes in planktonic assemblage in overlying water. For instance, proportional sterol abundances or ratios such as the proportion of dinosterol or the ratio of dinosterol to 24-methylcholesta-5,24(28)-dien-3β-ol have been used to track changes in the relative abundance of dinoflagellates, or the ratio of dinoflagellates to diatoms (e.g. Xing et al., 2011). Likewise, the alkenone to 24-methylcholesta-5,24(28)-dien-3β-ol ratio has been used as a proxy for the coccolithophorid to diatom ratio (e.g. Werne et al., 2000; Pourmand et al., 2007; Xing et al., 2011). Although biomarker distributions in suspended particulate matter (SPM; Ackman et al., 1968; Lee and Wakeham, 1988) and sinking particles (Wakeham and Lee, 1989; Canuel and Zimmerman, 1999; Prahl et al., 2000) have been observed to reflect primary productivity in oceanic surface water, extensive degradation of lipids occurs throughout the water column (Wakeham and Lee, 1993) and after burial during early diagenesis (Hedges and Prahl, 1993; Canuel and Martens,

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1996; Harvey and Macko, 1997). Therefore, knowledge of the relationship between biomarker production and preservation is essential before biomarker accumulation rates or assemblages can be used to interpret productivity and community variation in the past.

Several studies have compared biomarker distributions in the water column (either as suspended or sinking particulate matter) to those in underlying sediments in different oceanographic regimes to assess the reactivity of different compound classes (e.g. Wakeham et al., 1997, 2002; Prahl et al., 2000; Hernandez-Sanchez et al., 2012). Generally, long chain alkenones appear to be better preserved than sterols or short chain fatty acids (Cranwell, 1981; Sun and Wakeham, 1994; Wakeham et al., 1997; Hernandez-Sanchez et al., 2012), but the factors which determine the selective preservation of these compounds are not completely understood.

The reactivity of different compound classes is variable and depends on their structures (e.g. elemental composition or presence of functional groups; Sollins et al., 1996; Hedges and Oades, 1997). In addition, several environmental factors might govern the degree of organic matter (OM)/biomarker preservation, and thus the distribution of different biomarker classes in sediments (Wakeham and Canuel, 2006; Zonneveld et al., 2010). These factors include OM/biomarker supply from the upper ocean (Calvert and Pedersen, 1992), association with minerals and their surface area (Keil et al., 1994a,b), the existence of macromolecular protective matrices or O_2 exposure time/content in pore water (Zonneveld et al., 2010 and references therein). Additionally, the presence of macrofauna might have a direct impact on lipid preservation in sediments via bioturbation (Levin et al., 1997), remineralization (Zonneveld et al., 2010) and selective feeding (Sun et al., 1999).

In particular, O_2 exposure time/content of porewater has been shown to result in markedly different biomarker preservation response during field studies performed in areas where O_2 concentration varies drastically (e.g. oxic to anoxic sediments in Arabian Sea and Santa Monica Basin sediments and in Madeira Abyssal Plain turbidites; Gong and Hollander, 1999; Hoefs et al., 2002; Sinninghe Damsté et al., 2002). These studies evaluated biomarker and OM reactivity by either (i) comparing sedimentary horizons with a very different redox history within the same sedimentary record (e.g. turbidites in Madeira Abyssal Plain; Hoefs et al., 2002) or (ii) by comparing same time slices among different sediment cores underlying areas of similar export productivity that experienced different (bottom water) redox conditions (e.g. anoxic vs. oxic or oxic vs. suboxic) at the time of deposition (e.g. Arabian Sea; Sinninghe Damsté et al., 2002). Consequently, the effect of more nuanced differences (e.g. oxic vs. nitrogenous–ferruginous) in sedimentary O_2 concentration on biomarker preservation is less clear.

In this study we compare algal biomarker distributions in suspended particulate matter (SPM) collected from the upper water column (including the upper mixed layer) with those in underlying sediment core tops collected at 7 stations across a transect in the southwestern Cape Basin. The transect included the shelf-slope-basin transition, and therefore a range of porewater redox conditions from oxic to nitrogenous–ferruginous. In contrast to previous studies (Sinninghe-Damsté et al., 2002), all sediments were under a fully oxic water column. The dataset allowed us to evaluate the reactivity of different compound classes and to determine the effect of porewater redox state on lipid preservation. This builds on previous work (Sinninghe Damsté et al., 2002), based on proxy data, which evaluated the effect of bottom water, and therefore sediment–water interface redox conditions, on lipid preservation within sediments. Our study sheds further light on the biogeochemical processes that govern biomarker preservation in the oceanic water column and sediments and provides additional constraints on the use of sedimentary biomarker distributions as proxies for past oceanic conditions.

2. Methods

2.1. Study site

The South Atlantic Ocean transect (around 40°S; Fig. 1) is characterized by relatively high productivity, with satellite derived chlorophyll-*a* concentration (chl-*a*; monthly averaged SeaWifs concentration for the sampling period: October/November 2010; Ocean Color NASA) ranging from 0.2 to 0.4 mg/m^3 within southwestern Cape Basin waters [Stations (Sts.)1, 3, 4.5 and 6; Fig. 1] and even higher chl-*a* concentration observed nearshore (2.8 mg/m at Sts. 0.5 and 0.75), particularly within water overlying the Cape Shelf (e.g. 3 mg/m at St. 0; Fig. 1). The eastern part of the basin is influenced by the Agulhas leakage, with a weak upwelling cell north of Cape Town (Shannon, 1985; Lutjeharms and Meeuwis, 1987; Supplementary Fig. 1a). Associated with the upwelling cell, a front develops at the shelf break off the Cape Peninsula, which is particularly strong in summer (e.g. strong upwelling and advection of warm Agulhas current water offshore; Shelton and Hutchings, 1990). Associated with the upwelling front, a current flows northwards around the Cape Peninsula (Cape Jet; Shelton and Hutchings, 1982). This circulation pattern makes the coastal area south of Cape Town a dynamic oceanographic regime. In contrast, the hydrography offshore is more stable (Hardman-Mountford et al., 2003) and is predominantly under the influence of the subtropical front. Deeper water at this latitude consists of several distinct water masses: Antarctic Bottom Water (AABW), North Atlantic Deep Water (NADW) and Antarctic Intermediate Water (AIW; Supplementary Fig. 1b).

The transect spanned the shelf-slope-basin transition (St. 0 on the shelf, St. 0.5 and St. 0.75 on the slope; Sts. 1, 3, 4.5 and 6 in the Basin; Fig. 1), such that the sediments were deposited at increasing water depth (246 m at St. 0 to 5269 m at St. 4.5; Table 1) and under a range of bottom water O_2 concentration (Table 1). O_2 penetration depth varied from 0.65 cm on the shelf slope to > 5.4 cm in the Cape Basin (Hernandez-Sanchez et al., 2014; Table 1).

2.2. SPM and sediments

Water column and sediment samples were collected on the RRS Discovery (D357) in October–November 2010 on a cruise occupying section GA10 of the UK-GEOTRACES programme. During the cruise, mixed layer depth ranged from 35 m at nearshore stations to 150 m at the most distal stations (e.g. St. 6; Table 1) and chl-*a* maximum (chl-*a* max) also varied from 0–30 m to 60 m along the transect (Table 1).

SPM was collected using in situ stand alone pumps (SAPS) from multiple depths in the upper 200 m at the four offshore stations (20 and 200 m at St. 1; 10, 100 and 200 m at St. 3; 10 and 200 m at St. 4.5; 10, 60, 100 and 200 m at St. 6; Fig. 2) and only at the surface (ca. 5 m depth) at St. 0, St.0.5 and St. 0.75. SAPS were deployed for 0.5 to 2 h, and filtered 200-500 l seawater. The filters comprised two ashed and stacked glass fibre filters (GF/F 293 mm, nominal pore size 0.7 μm). Immediately after collection, filters were individually wrapped in Al foil and stored at −80 °C.

A combination of Bowers Connelly mega core and box core subsampling techniques were used to collect intact surface sediment cores (ca. 30 cm) from all stations. Cores were sliced at 1 or 2 cm intervals down to 10 cm below the seafloor (cmbsf), and each slice was individually wrapped in Al foil and stored at −20 °C until analysis. Only the sediment core tops (top 10 cm) were analysed for this study.