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Signature of organic matter exported from naturally Fe-fertilised oceanic waters

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ABSTRACT

Biomarker distributions and organic carbon and nitrogen isotopic signatures of organic matter (OM) produced in surface waters around the Crozet Plateau (Southern Ocean) are significantly different between a Fe-fertilised region (north) and a high nutrient low chlorophyll region (HNLC, south). If these OM signatures are exported to and preserved in surface sediments, they could potentially be used as palaeo-proxies for identifying Fe-fertilisation events in the past. Here, we assess the alteration of the OM signature through the water column and at the sediment–water interface by comparing organic signatures in surface waters, sediment traps and surface sediments. Our results suggest that there is significant degradation of OM during transport to the sea floor, which causes reduced fluxes of biomarkers to sediments north and east of the Crozet Plateau. Sterols, alkenones and C_{27} and C_{29} 12-hydroxymethyl alkanoates, and C_{28} 1,14-diols appear to be less labile than total organic carbon (TOC), except to the north, where alkenones and sterols are more rapidly degraded than TOC. Sedimentary bulk and compound specific $\delta^{13}C$ values also reflect surface water productivity patterns, with elevated values occurring in sediments underlying the Fe-fertilised waters. In contrast, $\delta^{15}N$ values appear to be strongly biased by degradation and grazing during export and burial. Thus, only some of the differences observed in surface waters between the Fe- fertilised and HNLC areas are exported to deep waters and preserved in the sedimentary record, suggesting that caution is required in the application of these proxies to studies of ocean palaeoproductivity.

1. Introduction

The Southern Ocean (SO) is largely characterised by low primary productivity and algal biomass, despite high concentrations of macronutrients, and is classified as a region of high nutrient low chlorophyll (HNLC). Phytoplankton growth in HNLC areas is thought to be limited by a combination of iron concentration and/or bioavailability (Martin, 1990; Martin et al., 1994; De Baar et al., 1995), light (Mitchell et al., 1991; Nelson and Smith, 1991), Si availability (Franck et al., 2000) or grazing (Morel et al., 1994). In the SO, iron enrichment experiments, such as SOIREE (Boyd et al., 2000), EinsenEx (Gervais et al., 2002), SOFeX (Coale et al., 2004) and EIFEX (Hoffmann et al., 2006), have provided strong evidence that iron bioavailability is an important control on phytoplankton growth and that low iron concentrations are growth-limiting (Cooper et al., 1996; Frew et al., 2001; Gall et al., 2001; Gervais et al., 2002). However, during these experiments, there has been no strong evidence for elevated export flux associated with the increase in phytoplankton biomass in surface waters (De Baar et al., 1995; Boyd et al., 2007). This was possibly the result of the temporally limited aspect of the project, as there is a lag of 20–30 days between OM formation and export, and most experiments lasted only 12–24 days (Buesseler et al., 2004). Lateral dilution of the iron infused path could also have influenced the measurements.

An alternative approach is to examine naturally iron-fertilised areas associated with island-systems in the SO (Pollard et al., 2007b; Blain et al., 2007). One such region is the Crozet Plateau (Indian sector of the SO), where export estimates (from ^{234}Th at 100 m) are three-fold higher than in the surrounding HNLC waters (Pollard et al., 2009). Thus, there is strong evidence that

Abbreviations: OM, organic matter; TOC, total organic carbon; HNLC, high nutrients low chlorophyll; SO, Southern Ocean; ACC, Antarctic Circumpolar Current; TLE, total lipid extract; SAPS, stand alone pump systems; AMS, accelerator mass spectrometry; SUERC, Scottish Universities Environmental Research Centre

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natural Fe fertilisation increases the strength of the biological pump. However, we currently have little understanding of how this sinking organic matter is altered in the Crozet region or preserved in underlying sediments. The iron-induced bloom north of the Crozet Plateau is associated with distinct biomarker assemblages and carbon and nitrogen isotopic signatures (Hernandez et al., 2008; Hernandez-Sanchez et al., 2010). Previous work has shown that organic matter exported from surface waters can be altered through the water column and in surface sediments (Canuel and Martens, 1996; Harvey and Macko, 1997), with more labile compounds being preferentially degraded during water column transport (Harvey and Macko, 1997). Although lipids are less reactive than other compounds and can potentially be used as biomarkers (Volkman et al., 1987; Wakeham and Lee., 1993), they also degrade at different rates depending on the depositional environment (e.g. McCaffrey et al., 1991; Sun and Wakeham, 1994; Sun et al., 1997; Hoefs et al., 2002). Additionally, lipid distributions are also influenced by bioturbation at the sediment–water interface (Sun and Wakeham, 1999).

However, these processes remain poorly understood and there are few studies that have specifically compared surface water and sediment trap biomarker assemblages and those preserved in underlying sediments (Prahl et al., 1993; Wakeham et al., 1997, 2002; Prahl et al., 2000). Thus, there is a need to characterise biomarker degradation/preservation in specific oceanographic regimes, if they are to be used to test export productivity (iron-stimulated in this study) in the past and to understand the relationship between phytoplankton growth and export productivity. This paper has three primary objectives all arising from analyses of surface sediments and deep water sediment traps from the same sites as the surface water samples as described by Hernandez-Sanchez et al. (2010). The primary aim is to evaluate changes in the organic matter signature (biomarker distributions and isotopic values) between surface waters, deep-ocean sediment traps (~2000–3000 m) and the sediment–water interface (~3200–4200 m). Second, we assess whether or not regional differences identified in Crozet waters by Hernandez-Sanchez et al. (2010) are reflected in traps and sediments. The third and ultimate aim is to understand the fidelity with which the signature of organic matter in sediments record surface water and/or export production.

2. Methodology

2.1. Oceanographic setting

The Crozet Plateau is located in the Indian sector of the SO (45–47°S, 49–51°E; Fig. 1). In this area, the Antarctic Circumpolar Current (ACC) is diverted to the north as a result of the bathymetry (Pollard et al., 2007a) and as a consequence the area between the ACC and the Crozet Islands (to the North) is hydrographically constrained and currents are slack (Pollard et al., 2007b). Over winter, this area is fertilised by Fe sourced from the Crozet Plateau (Planquette et al., 2007) and an algal bloom is observed each year with the onset of improving light conditions and stratification early in the austral summer (Venables et al., 2007).

2.2. Samples

2.2.1. Sediment traps

Because our focus is on OM that has been exported to the deep ocean and shallow waters are subjected to remineralisation between 100 and 1000 m (Martin et al., 1987; Buesseler et al., 2007), we focussed on sediment traps deployed at depths

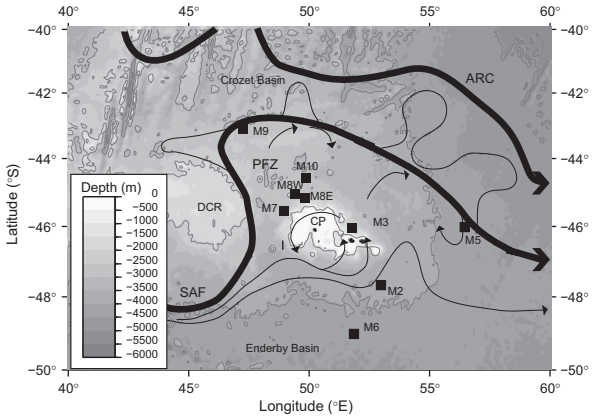

Fig. 1. Bathymetry and stations sampled around the Plateau: M10, M3, M5 and M6. Crozet Plateau (CP) and Del Caño Rise (DCR) are also indicated. Black lines illustrate the circulation pattern around the Plateau described by Pollard et al. (2007b): the thick lines represent the Agulas Return Current (ARC) and the Sub Antarctic Front (SAF), with thinner lines marking transient eddies. The thin lines with the arrows illustrate the very weak circulation in the Polar Frontal Zone (PFZ) between the Sub Antarctic Front (SAF) and the Crozet Plateau.

> 1000 m. A set of McLane sediment traps (21 cups) was deployed around the Plateau (Fig. 1) during a cruise (D286) in austral summer 2004–2005 at M10 (2000 m), M5 (3195 m) and M6 (3160 m) and recovered during a second cruise (D300), which took place in December 2005–January 2006 recovering 94%, 97% and 96% of the annual flux (late December 2004/January 2005 to December 2005; Pollard et al., 2009), respectively. Sediment trap cups (250 mL) were filled with preservative solution (100 g of NaCl in 19 L of unfiltered deep seawater; Salter et al., 2012), and swimmers, fish debris and scales were removed from the samples prior to analysis. A few of the samples were heavily contaminated by fish debris (Table 1). The 250 mL samples were split into 8 equal aliquots using a rotary splitter and each of the aliquots was filtered through two stacked GF/F filters and frozen (-50°C) prior to analysis.

2.2.2. Surface sediments

Two short mega-cores were recovered from station M5 (4269 m) and M6 (4268 m) during austral summer 2004/2005. Additionally, a mega core was collected from station M10 (3227 m) during austral summer 2005/2006. Following extensive echo sounding during D300 (austral summer 2005/2006), it was noted that the coring site at M5 chosen during D286 in austral summer 2004/2005 was likely to have been taken from a channel and therefore, it may have been influenced by down-slope as well as pelagic sedimentation. Mega-cores were sliced into 1–2 cm slices and frozen after recovery; the top 2 cm were used for this study. Sediment samples are primarily composed of opaline silica and calcium carbonate, with a significant component of lithogenic material (Marsh et al., 2007). Sedimentation rates range from 1 to 5.5 cm kyr^{-1} (Marsh et al., 2007) so that a typical 1–2 cm surface sediment slice represents from 500 to 19,000 years. It is crucial to note, therefore, that although sediment traps record the OM flux for less than a single year, sedimentary geochemical signatures have been integrated over much longer time intervals; this could be crucial for geographical comparisons because the current location HNLC area to the south of the Plateau might not have been persistent throughout the Holocene.

2.3. Biomarker analysis

Freeze dried GF/F filters containing sediment trap material were extracted in an ultrasonic bath for 45 min with a 9:1 (v/v)