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Deep-Sea Research I 52 (2005) 721–748
DEEP-SEA RESEARCH PART I
www.elsevier.com/locate/dsr

Alkenone temperature records and biomarker flux at the subtropical front on the chatham rise, SW Pacific Ocean

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Received 19 April 2004; received in revised form 12 November 2004; accepted 13 December 2004

Abstract

Alkenones and a suite of sterol biomarkers were examined in two sediment trap arrays deployed at 300 m depth in subtropical and subantarctic waters to the east of New Zealand from late winter to autumn in 1996–1997. The two traps were located within 200 km of one another and the main difference between the two sites are the differential physical, chemical, and biological characteristics of the different water masses in which they were situated. The alkenone-based reconstructions of water temperatures ($U^{K'}_{37}$) were compared to the COADS monthly averaged satellite and real-time weekly temperatures for the deployment period. The records correlate well with seasonal sea surface temperatures (SST) for the 9 months of the deployment, with temperature reconstructions within 2 °C of regional monthly averages for most of the year. There are a few short periods of poorer agreement where alkenone-based reconstructions deviate by up to 4 °C in both traps. Weekly averages of satellite SST obtained during the time of the deployment indicate that these deviations were not associated with short-term changes in surface temperatures overlying the traps. These instances of poor correlation are not due to lateral advection of particles, but rather seem to reflect differences in environmental controls on alkenone-derived SSTs in the two water masses. Subantarctic traps showed deviations only to warmer than average temperatures. These occurred in early winter and late summer, during times of low lipid fluxes, suggesting that slow growth associated with light limitation may have affected unsaturation levels in the alkenones. The subtropical traps showed deviations only to cooler temperatures, which occurred in the late summer to early autumn. These biases occurred during times of highest lipid fluxes and lowest nutrients in the surface mixed-layer. Alkenone temperatures during maximum flux periods were too cool to be caused by subsurface production alone, suggesting that nutrient limitation effects may have significantly depressed alkenone unsaturation levels. Sterol biomarker associations indicate very different timing and trophic interactions between phytoplankton in the respective water masses. In subtropical waters, fluxes of dinosterol (a biomarker for dinoflagellates) peak first in the spring bloom while alkenones and diatom

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0967-0637/$ - see front matter
doi:10.1016/j.dsr.2004.12.003

marker sterols respond synchronously during the main bloom event. In subantarctic waters sterol fluxes indicate a succession of phytoplankton export production in the spring bloom, whereas lipid fluxes normalized to organic flux indicate that alkenone producers were a relatively small proportion of the main spring bloom and proportionally more important when organic fluxes were lower in summer. We infer that the difference in nutrient concentrations between the water masses may drive these trophic differences and the inverse relationship between flux and the temperature response of $U^{K'}_{37}$ between the two sites.

Keywords: Alkenones; $U^{K'}_{37}$; Lipids; Sea surface temperature; Sediment traps; Southern ocean; Sterols

1. Introduction

The C_{37-39} alkenones are biosynthesized by a very few species of haptophyte phytoplankton, including the cosmopolitan coccolithophore *Emiliania huxley*i and the subtropical *Gephyrocapsa oceanica* in the open ocean (Conte et al., 1998a, 1994b; Volkman et al., 1995, 1980a, b). Consequently, alkenones are true biomarkers for a well-defined portion of surface productivity in the world ocean. These alkenones have either 2, 3, or 4 double bonds (although trace amounts of mono-unsaturated alkenones have recently been detected (Rontani et al., 2001). The degree of unsaturation of the C_{37} alkenones has been shown to increase with decreasing temperature of the water in which the microalgae grow (Brassell et al., 1986; Marlowe, 1984; Prahl and Wakeham, 1987) and the unsaturation in a sample correlates well with growth temperatures (Prahl and Wakeham, 1987). For temperature estimation, this unsaturation is generally expressed as the $U^{K'}_{37}$ ratio, which is the ratio of the amount of di-unsaturated to the total di- plus tri-unsaturated C_{37} alkenones in the sample ([37:2]/[37:2 + 37:3]).

Over the last 15 years, alkenone unsaturation has become an increasingly widespread technique to reconstruct paleotemperatures from deep ocean sediment cores. The record of $U^{K'}_{37}$ in the sediments correlates well to sea surface temperature (SST) and has proven reliable and robust in reconstructing past SST (see Herbert, 2001, for a review). Despite this robustness, there are still many unanswered questions as to why $U^{K'}_{37}$-inferred temperatures do not always match SST values. In laboratory cultures, different strains of alkenone producers often produce relationships more dissimilar to temperature than those derived from field studies (Conte et al., 1994a, 1998a; Epstein et al., 2001, 1998a; Herbert, 2001; Popp et al., 1998; Prahl et al., 2003; Versteegh et al., 2001; Volkman et al., 1995). Different responses to apparently identical culture conditions have been noted (e.g. Epstein et al., 1998a; Popp et al., 1998) which often do not correlate well with the response of the same organisms in the open ocean (Conte et al., 1998a; Epstein et al., 2001; Volkman et al., 1995). Culture and field studies have also demonstrated that environmental factors such as nutrient stress, light levels, and changes in growth rate may influence $U^{K'}_{37}$ values (e.g. Conte et al., 1998a; Epstein et al., 2001, 1998b; Popp et al., 1998; Versteegh et al., 2001; see Herbert, 2001; Laws et al., 2001; Prahl et al., 2003, 2000a for reviews). Additionally, results from some culture studies indicate that phosphate and light limitation are an important secondary factor in controlling alkenone unsaturation levels (Epstein et al., 2001; Versteegh et al., 2001). Importantly, recent evidence from *E. huxleyi* cultures (the main producer of alkenones in the open ocean) shows clearly that low nitrate and phosphate levels lead to lower $U^{K'}_{37}$ ratios whereas low light levels are associated with increased $U^{K'}_{37}$ values, producing temperature reconstructions that are a few degrees "too cold" or "too warm", respectively, for the water temperatures in which the haptophytes grew (Prahl et al., 2003). This information can be used to understand data from previous field studies.

Oceanographic studies from the water column generally show a strong and consistent correlation of $U^{K'}_{37}$ to growth temperature (Conte et al., 2001; Prahl and Wakeham, 1987; Sicre et al., 2002; Sikes and Volkman, 1993). Sediment trap studies

indicate that alkenone production is highly seasonal and that subsurface production may be important (Harada et al., 2001; Prahl et al., 1993; Ternois et al., 1997, 1996). This implies that episodic production and sedimentation events may strongly influence fluxes to the sediment and the resulting temperature record preserved there (Müller and Fischer, 2001). Results from some in situ studies do show poor SST-$U^{K'}_{37}$ correlations (Conte and Eglinton, 1993) suggesting that in certain situations, the relationship to temperature does not conform to established calibrations while other studies indicate that $U^{K'}_{37}$ values show bias reflecting the season and depth of growth (e.g. Ohkouchi et al., 1999; Prahl et al., 1993, 1995; Sikes et al., 1997).

$U^{K'}_{37}$ values measured in sediment traps record the short-term and seasonal response of the alkenone producers to mixed layer temperatures. Sediment-trap-based temperature reconstructions from a broad range of open ocean, coastal, and frontal locations, however, often return temperatures that do not agree with recorded sea surface temperature during times of high or maximum flux (Goñi et al., 2001; Harada et al., 2001; Müller and Fischer, 2001; Prahl et al., 1993, 2001; Rosell-Melé et al., 2000; Ternois et al., 1997, 1996). Occasionally, temperature reconstructions are too warm for a given season (Goñi et al., 2001; Prahl et al., 2000b), but generally anomalous temperature reconstructions from trap material are cooler by ~1–4 °C than actual SST. In some locations, exported alkenones have a cool temperature offset that is so large that temperatures represented in traps (Prahl et al., 1993) and sediments (Ohkouchi et al., 1999) reflect the lower limit of the annual range in SST. These differences are not due to calibration deviations, but rather result from alkenone production at the base of the surface mixed-layer (Harada et al., 2001; Prahl et al., 1993, 2001; Ternois et al., 1997, 1996), or to lateral transport by surface currents (Rosell-Melé et al., 2000) Production at the base of the surface mixed layer is supported by detailed water column analyses in the Mediterranean (Bentaleb and Fontugne, 1998; Ternois et al., 1997).

A cool bias in alkenones being delivered to the sediments does not mean that production-weighted annual average temperature reconstructions return temperatures cooler than annual surface temperature means. This point is often overlooked because the times when the alkenone temperature response does not match SST are often short-lived in the annual cycle. Consequently, when trap-based reconstructions are averaged over an annual cycle, they often equal annual average temperatures (Müller and Fischer, 2001; Prahl et al., 2001). Notably, this often agrees with underlying sediments (Müller and Fischer, 2001; Prahl et al., 2001) and agrees with the most accepted interpretation of the world-wide sediment calibration (Müller et al., 1998; Prahl et al., 2000a). Thus, temperature reconstructions from trap derived flux-weighted annual averages fit readily with expectations from sediment calibrations.

Despite this numerical agreement between trap annual averages and underlying sediments, the overwhelming evidence is that alkenones are not produced in "annual average" conditions. Trap studies clearly show that maximum flux often occurs in a single season and not evenly throughout the year. Outside the tropics the growth season is generally the spring and early summer, a time when SST is warmer than annual average (e.g. Müller and Fischer, 2001; Prahl et al., 1993; Rosell-Melé et al., 2000; Ternois et al., 1998, 1997). This scenario suggests that single bloom events with $U^{K'}_{37}$ levels that differ from calibrations may be driving the alkenone record preserved in the sediments (Müller and Fischer, 2001). In light of this, it is not surprising that comparisons of studies for which growth temperatures were fully determined, that is, correlations using water column samples (Sikes and Sicre, 2002; Sikes and Volkman, 1993; Sikes et al., 1997) and the culture correlation of Prahl et al. (1988), which is the standard in the field, agree best with sediment correlations for the summer season (Müller et al., 1998; Sikes et al., 1997). Correlations with any other season, or the annual average temperature, agree less well (Sikes et al., 1997).

These sediment trap records illustrate that the $U^{K'}_{37}$ temperature signal delivered to the sediments often does not record the SST at the time of maximum flux to the sediments, which can

potentially bias paleo-records. This observation has important implications for paleoceanographic reconstructions of past SSTs. Although alkenone-derived temperatures consistently agree with other paleo-SST proxies in modern sediments (e.g. Chapman et al., 1996; Pichon et al., 1998; Sikes et al., 2002; Sikes and Keigwin, 1994), alkenone-based reconstructions can disagree with other paleotemperature estimators during times when environmental conditions such as thermocline depth and seasonality were different from the present (e.g. Chapman et al., 1996; Sicre et al., 2001, 2002; Sikes and Keigwin, 1994, 1996; Weaver et al., 1999). In the New Zealand region, the SST reconstructions of the last glacial cycle vary significantly when measured with proxies based on alkenones or coccolith or foraminiferal assemblages (Barrows et al., 2000; Sikes et al., 2002; Weaver et al., 1998, 1997; Wells and Okada, 1997), leaving the magnitude of the glacial temperature change in this region uncertain. Previous analysis suggests that foraminifera reconstructions may be biased in the New Zealand region (Barrows et al., 2000; Wells and Okada, 1997). Accordingly, it is essential to examine the environmental conditions associated with alkenone sedimentation and the SST record.

1.1. Study area and regional setting

Biomarker fluxes were determined from two trap arrays deployed to the east of New Zealand on the north and south flanks of the Chatham Rise. Placement of the arrays on the Chatham Rise permitted the traps to be closely situated and subject to the same weather conditions but to sit in two different water masses: low macro-nutrient, oligotrophic to mesotrophic subtropical waters in the north and micronutrient-limited subantarctic waters with high macro-nutrients to the south. The water masses are separated by the Subtropical Front (STF) which sits astride the Chatham Rise, a 1500 km long submerged continental ridge at ~44°S to the east of New Zealand (Fig. 1).

The Subtropical Front is considered to be the northern extent of the Southern Ocean, marking the boundary between subtropical and subantarctic waters. The subtropical surface waters to the north of the STF are mesootrophic, warm, and saltier (about 35.4 in this location) and flow south in the East Auckland and East Cape currents from the South Pacific Gyre along the eastern continental margin to the Chatham Rise (Fig. 1). Subantarctic waters are nutrient-rich and salinities are lower (around 34.5) (Butler et al., 1992). The surface water temperature south to north across the front varies on average from 10 to 14 °C in the winter to 14 and 18 °C in the summer (cf. Belkin and Gordon, 1996; Chiswell, 1994b, 2003; Sutton, 2001; Uddstrom and Oien, 1999).

The STF is an area with strong mesoscale variability with exact location of the front the subject of debate. There are numerous regional currents associated with both the STF at the surface and with deep western boundary currents on the flanks of the plateaus in the area. Surface currents in the area parallel the eastern coastlines of the New Zealand land mass and converge upon the Rise: the Southland Current delivers cool water to the southern flank of the Chatham Rise, while the East Cape Current delivers warm waters to the north. These coalesce into eastward flow within the STF along the Chatham Rise (Chiswell, 1994a, b; Uddstrom and Oien, 1999) (Fig. 1). It has been suggested that the STF on the Chatham Rise comprises two main frontal systems as in other areas of the Southern Ocean, with both a north STF running along the northern flank of the rise and a south STF running along the southern crest of the rise (Belkin and Gordon, 1996). Regional studies on the Chatham Rise have failed to resolve a double front, suggesting instead that the front migrates north–south across the Chatham Rise on a seasonal basis (Chiswell, 1994b), or alternatively, that the front sits consistently to the south of the rise, and variability to the north is associated with the Wairarapa Eddy, which is associated with the East Cape Current (Uddstrom and Oien, 1999) (Fig. 1).

The STF is an area of enhanced productivity (Bradford-Grieve et al., 1997) presumably associated with the mixing of subtropical and subantarctic waters. In situ water column studies on the Chatham Rise (Bradford-Grieve et al., 1999), sediment trap data (Nodder and Northcote, 2001), and satellite-derived chlorophyll data (Comiso

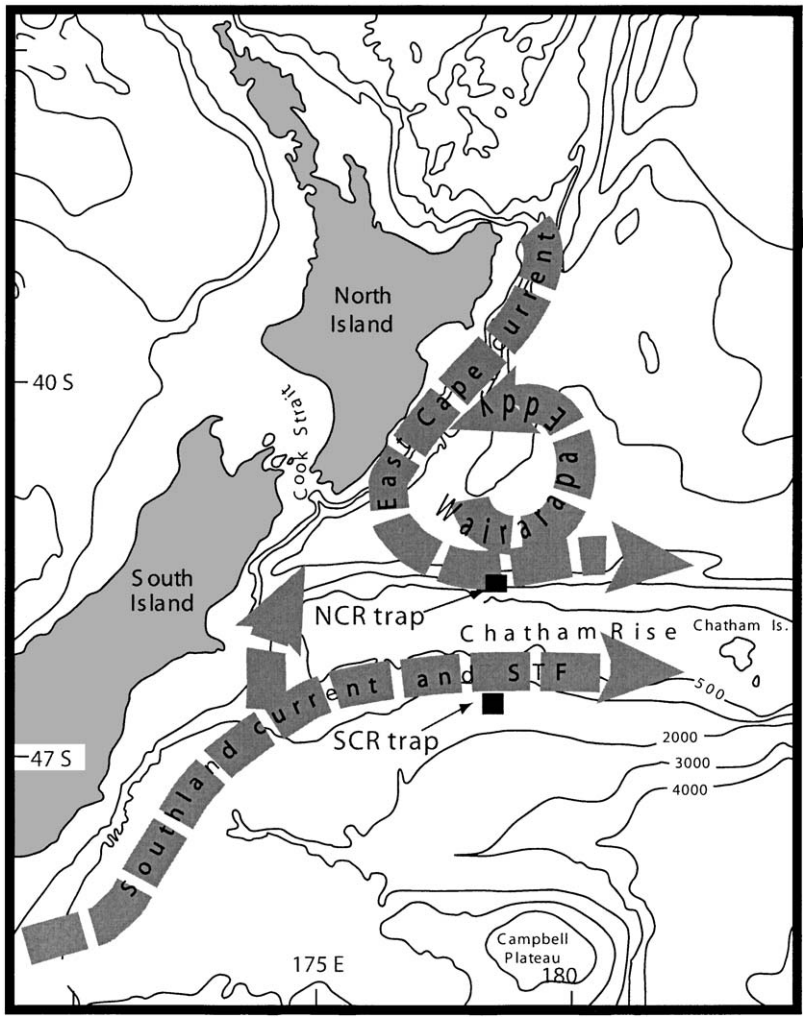


Fig. 1. Map of study site. Trap sites are indicated by solid squares. Surface currents bring subantarctic waters from the south to flow parallel to the south flank of the Chatham Rise. Likewise, subtropical waters from the north are delivered parallel to the north flank of the Chatham Rise with the exception of the existence of the semi-permanent Wairarapa Eddy which recirculates water at the west end of the Rise. Benthic currents parallel the bathymetry and follow the general direction of surface currents along the Chatham Rise. Despite strong flows, current meter and particle flux studies indicate little lateral transport north–south across the Rise (see discussion in text). The South Chatham Rise trap was deployed from 9 June 1996. The northern trap deployment was delayed until 14 September 1996, and both deployments ran until 15 May 1997.

et al., 1993; Murphy et al., 2001) all indicate that fluxes and productivity are substantially greater in spring–summer than in winter. Significantly, although blooms begin and sometimes peak in spring on the Chatham Rise (Nodder and Northcote, 2001), these blooms often persist into summer (January–March: Comiso et al., 1993; Nodder and Northcote, 2001). Subtropical waters to the north of the STF are characterized by strong seasonality in biological production, with large ($>20\,\mu m$) diatoms dominating spring blooms in the region (Bradford-Grieve et al., 1997; Chang and Gall, 1998; Murphy et al., 2001), especially when microzooplankton grazing becomes

decoupled from phytoplankton growth (James and Hall, 1998).

In contrast, subantarctic waters exhibit little seasonality in terms of chlorophyll *a* biomass (Banse and English, 1997; Bradford-Grieve et al., 1997; Murphy et al., 2001), with phytoplankton communities dominated by small phytoplankton cells ($<2\,\mu m$), which are iron-limited (Boyd et al., 1999). Distributions of the main alkenone producers, namely pymnesiophytes or coccolithophorids, in the New Zealand region are presently unknown, although recent satellite imagery (Boyd and Doney, 2003) and pigment biomarkers (specifically19′-hexanoloxyfucoxanthin) suggest that these organisms are present in subtropical, STF and subantarctic waters (Chang and Gall, 1998; Nodder and Gall, 1998).

Microzooplankton biomass is relatively constant across the Chatham Rise region (winter: 1–2 mg C m^{-3}, spring: 2–9 mg C m^{-3}) with grazing rates predominantly exceeding daily primary production rates, except in subtropical waters in spring (Hall et al., 2004; James and Hall, 1998). In contrast, mesozooplankton biomass in subtropical waters can contribute ~40% of the total plankton biomass in spring (winter: ~120 mg C m^{-2}, spring: ~2900 mg C m^{-2} (Bradford-Grieve et al., 1999) and graze 70% of phytoplankton growth (Hall et al., 2004), whereas in subantarctic waters there is little apparent seasonality (~300–390 mg C m^{-2}). Mesozooplankton grazing rates on phytoplankton are generally <4% of the daily primary production in all water masses to the east of New Zealand (Bradford-Grieve et al., 1998), although zooplankton fecal pellets are likely to be significant contributors to export flux in subtropical and STF waters in spring (Nodder and Gall, 1998).

1.2. Sterol biomarkers and environmental conditions

Sterols are found in all eukaryotes and in a few bacteria, but specific sterols can serve as indicators for categories of organisms, particularly in the marine environment. In addition to the alkenones, we have quantified the major sterols present in the traps to establish ecosystem characteristics during trap deployment. Of the major sterols in the traps, cholesterol (cholest-5-en-3β-ol) is generally considered a zooplankton indicator, although it is also synthesized by some species of phytoplankton (Volkman et al., 1998). Other major sterols such as cholesta-5,22E-dien-3β-ol (*trans*-22-dehydrocholesterol), epi-brassicasterol (24-methylcholesta-5,22E-dien-3β-ol), and desmosterol (cholesta-5,24-dien-3β-ol) are abundant in several species of marine diatoms (Barrett et al., 1995), although the latter is also found in some marine animals. 24-Methylenecholesterol (24-methylcholesta-5,24(28)-dien-3β-ol) is abundant in diatoms and more common in centric diatoms than in pennates (Barrett et al., 1995). Note that we, in common with almost all sterol studies, have not determined the C-24 stereochemistry of the alkyl group in C_{28} and C_{29} sterols, so the C_{28} $\Delta^{5,22}$ sterol could be either brassicasterol (24β) or epi-brassicasterol (24α) or a mixture of both. Since both diatoms and haptophytes synthesize the 24α isomer (Volkman et al., 1998), we have referred to this sterol as epi-brassicasterol (also called diatomsterol), recognizing that small amounts of the 24β isomer might be present.

To assist our interpretation of the alkenone time series temperature reconstructions, we compared these results with the environmental parameters temperature, nutrients, mixed layer depth, and, where available, fluorescence (as a proxy for chlorophyll *a* levels). The purpose was to determine if the alkenone temperature reconstructions from sediment trap samples were influenced by production deep in the mixed-layer, or by nutrient, light, or growth-rate effects as suggested by previous work with cultures. We examined a coordinated set of related fluxes (e.g., total flux, particulate organic carbon (POC), detailed in Nodder and Northcote, 2001) as well as associated sterols that serve as proxies for the export production of plankton to determine the influence that other plankton may have on the abundance of alkenone producers. Competition for available nutrients affects the trophic structure of a bloom, and alkenone producers are known to be outcompeted by larger phytoplankton, in particular diatoms. In nutrient-rich upwelling areas, for example, coccolithophores usually bloom after the main diatom bloom has passed (Mitchell-Innes and Winter, 1987; Ziveri and Thunell, 2000).

2. Methods

Two sediment trap arrays with traps at 300 and 1000 m were placed in 1500 m water depth north and south of the STF and the Chatham Rise in 1996. The southern sediment trap (SCR) was deployed in late May 1996 at 44°37′S, 178°37′E on the southern flank of the Chatham Rise. The northern mooring (NCR) was deployed in early September 1996 at 42°42′S, 178°38′E on the north flank of the Chatham Rise. Both moorings were equipped with McLane PARFLUX Mk 7G-21 time incremental traps. Sequential sampling was completed in late April, and traps were recovered in May 1997 (Nodder and Northcote, 2001). The traps sampled for lipid analyses were moored at 300 m, and the northern traps were programmed for 8 d sampling intervals during the predicted spring bloom period until December 1996 and then converted to 16-d sampling periods to coincide with the collection periods of the southern traps, which had a 16-d collection period for the full deployment. Several bottles from the northern traps covering November–December 1996 and late March (spring-summer) and one bottle from the southern trap covering late February were found to be broken upon recovery. Prior to deployment, trap sample bottles were filled with a borax-buffered, high-density NaCl brine (excess 5–6‰) and filtered seawater (<0.5 μm) with 0.3% $HgCl_2$ and 6% formalin solutions added to the northern and southern traps, respectively, to reduce microbial degradation of collected organic material (e.g., Knauer et al., 1984). Full information on instrumentation, current meter data, and sample recovery is detailed in Nodder and Northcote (2001), as are total flux and POC fluxes used for calculations in this study. Full information on instrumentation, current meter data, and sample recovery is detailed in Nodder and Northcote (2001), as are total flux and POC fluxes used for calculations in this study.

Upon recovery, 250 ml trap sample bottles were removed and refrigerated at 4 °C until subsampling ashore. Samples were washed through a 1 mm mesh and 333 μm screen to remove zooplankton "swimmers" and the remaining solution split with using a McLane wet splitter. It is probable that some microzooplankton would pass through these sieves and thus contribute lipids to the final sample, but we have no information on how important this contribution might be. Samples for lipid analysis were then filtered onto precombusted glass fiber filters (GFF) and frozen at −20 °C until extraction. Frozen filters were extracted ultrasonically in chloroform and methanol (3:1 v/v) to provide a total lipid extract, and saponified to isolate the neutral fraction following procedures in Sikes and Volkman (1993) and Volkman et al. (1988). After sample clean-up, the neutral fraction was derivatised with BSTFA to convert sterols to sterol TMSi-ethers and then analyzed by capillary GC using an HP-1 methyl silicone fused column (50 m × 0.32 mm id.) in an HP 5890 GC with a cooled on-column injector and hydrogen as the carrier gas. The temperature program was 50–150 °C at 30 °C min^{-1} and 150–325 °C at 3 °C min^{-1}, which ensured good separation of all major constituents. Compounds were detected with a flame ionization detector, and peak areas were calculated with DAPA acquisition and processing software.

"Total long-chain alkenones" comprise the sum of all the C_{37} (methyl) and C_{38} (ethyl) alkenones. Fluxes calculated for total alkenones were also normalized to total mass flux and POC flux as determined for that cup as reported in Nodder and Northcote, (2001). POC fluxes were prepared by acidifying with 8% v/v sulphurous acid (Verardo et al., 1990) We normalized alkenone and sterol fluxes to the POC flux as a measure of the relative proportion of organic flux that could be related to different groups of organisms. Sterol and alkenone amounts were calculated from the same chromatograms.

3. Results

3.1. Alkenone temperature reconstructions

$U^{K'}_{37}$ values were converted to temperatures according to the calibration of Sikes and Volkman (1993). Globally, the Prahl et al. (1988) calibration ($U^{K'}_{37} = 0.034T + 0.039$) is now considered the standard in the field, but it is not recommended for use where the calibration returns unrealistic

estimates (Prahl et al., 2000a). The Prahl et al. (1988) calibration produces temperatures that are 2–3 °C too cool for the New Zealand region in sediment–based reconstructions (Sikes et al., 2002). The Sikes and Volkman (1993) calibration ($U^{K'}_{37} = 0.0414T - 0.156$) utilizes a high proportion of Southern Ocean samples and produces temperature reconstructions in our trap samples that more closely match regional monthly SST means than the Prahl et al. (1988) calibration (Fig. 2, Table 1). The correlations here and in other high-latitude locations (Harada et al., 2003) suggest that this calibration is more appropriate for high latitude waters and polar waters in particular. As a further assessment of the correlation of alkenone temperature reconstructions to surface temperature and productivity to seasonal SST, we examined the fit of reconstructed temperatures to data shifted by 3 weeks against the COADS temperature record. This shift allows for an assumed settling time of the particles from the surface mixed layer to the traps at 300 m. This did improve the correlation of temperature reconstructions to monthly averages, but not enough to account for the discrepancy between reconstructed temperatures and satellite temperatures. Accordingly, we do not present any time-lagged data here.

The alkenone-based reconstructions of water temperature were compared to the COADS monthly averaged record of temperature for this region from satellite determinations (COADS, 1999). The records agree well for the 9 months of the deployment, reconstructing both the temperature range and cycle. Temperature reconstructions were within 2 °C over most of the deployment, with short periods with poorer agreement (within 4 °C) in both traps. Deviations to warmer than average temperatures occurred in the southern trap in early winter and late summer. Deviations to cooler temperatures occurred in the northern traps in late summer to early autumn. Notably, shifts to warmer temperatures occurred only in subpolar waters, whereas shifts to cooler temperatures occurred only in subtropical waters. (Fig. 2a and b).

Our trap sites are located either side of the average location of the Subtropical Front, which is well known to have large mesoscale eddies that might deliver waters that cause SST to deviate by 2–4 °C from regional averages on the order of a few days (Roemmich and Sutton, 1998; Uddstrom and Oien, 1999). Delivery of warm water to the northern trap site is particularly likely due to the persistence of the Wairarapa Eddy (Chiswell, 2003; Roemmich and Sutton, 1998; Sutton, 2001). To assess the influence of eddies and short-term temperature anomalies due to mesoscale features for the period of trap deployment, we obtained weekly averages of regional satellite SSTs and concentrated on time periods when $U^{K'}_{37}$ temperatures from trap reconstructions deviated from regional means (COADS, 1999; see Fig. 2) and also for the three 1-week periods preceding those times to account for settling time. In none of the cases where $U^{K'}_{37}$ temperature reconstructions varied from regional averages did we detect

Fig. 2. Alkenone fluxes and SST reconstructions for 1996–1997 trap deployment. Solid lines are COADS temperature data for the latitudes associated with the trap locations. Dotted lines are alkenone-SST reconstructions, solid lines with symbols are absolute fluxes. Dashed lines are alkenone fluxes normalized to POC; dashed dotted lines are alkenone fluxes normalized to total fluxes: (a) Temperature reconstruction and alkenone fluxes for the north trap (deployed in subtropical waters) plotted with COADS monthly mean temperatures for both the north and south trap location for reference. (b) Alkenone fluxes for the north trap. Plotted are absolute fluxes and fluxes normalized to total mass flux and particulate organic carbon (POC) flux. COADS monthly mean temperatures for the trap location are plotted for reference. (c) Temperature reconstructions and alkenone fluxes for the south trap (deployed in subantarctic waters), plotted with COADS monthly mean temperatures for both the north and south trap location for reference. (d) Alkenone fluxes for the south trap. Plotted are absolute fluxes and fluxes normalized to total mass flux and POC flux. COADS monthly mean temperatures for the trap location is plotted for reference. Alkenone-SST reconstructions match actual SST for periods of relatively low flux in the subtropical (low nutrient) trap and are not consistently associated with high fluxes for the subantarctic (high nutrient) trap. Temperatures have been converted from $U^{K'}_{37}$ using the Sikes and Volkman (1993) calibration ($U^{K'}_{37} = 0.0414T - 0.156$). The Prahl et al. (1988) calibration produces temperatures that are consistently 4 °C too cold to be considered realistic. COADS annual average temperature is 15.5 and 11.5 °C for the northern and southern sites, respectively. Flux weighted average temperature reconstructions for 1996–1997 are 14 and 11 °C, north and south, respectively.

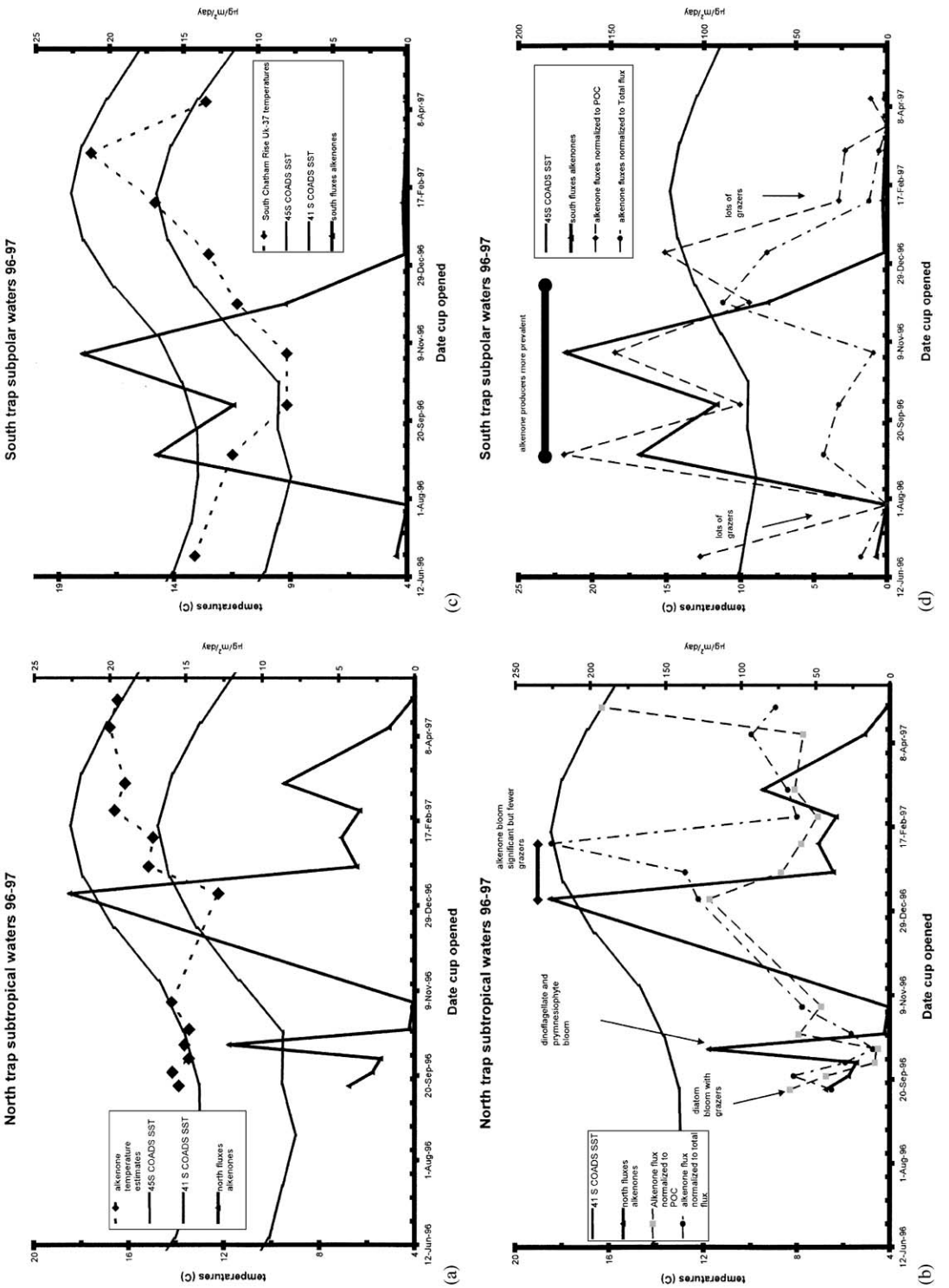

North trap subtropical waters 96-97
South trap subpolar waters 96-97
temperatures (C)
Date cup opened
12-Jun-96
1-Aug-96
20-Sep-96
9-Nov-96
29-Dec-96
17-Feb-97
8-Apr-97
alkenone temperature estimates
45S COADS SST
41 S COADS SST
north fluxes alkenones
South Chatham Rise Uk-37 temperatures
south fluxes alkenones
alkenone producers more prevalent
lots of grazers
alkenone fluxes normalized to POC
alkenone fluxes normalized to Total flux
alkenone bloom significant but fewer grazers
dinoflagellate and prymnesiophyte bloom
diatom bloom with grazers
Alkenone flux normalized to POC
alkenone flux normalized to total flux
(a)
(b)
(c)
(d)

Table 1
$U^{K'}_{37}$ and SST reconstructions for individual sediment trap cups

Date cup opened	$U^{K'}_{37}$	Temperature reconstructions, T (°C)		COADS SST, T (°C)	Monthly average
		Prahl et al., 1988	Sikes and Volkman, 1993		
	North Chatham Rise			45°S	
14 September 1996	0.419	11.2	13.9	9.6	September
22 September 1996	0.430	11.5	14.2	9.6	September
30September-1996	0.401	10.7	13.5	9.6	September
08 October 1996	0.409	10.9	13.6	9.5	October
17 October 1996	0.400	10.6	13.4	9.5	October
02 November 1996	0.431	11.5	14.2	11.4	November
05 January 1997	0.350	9.1	12.2	14.3	January
21 January 1997	0.472	12.7	15.2	14.3	January
7 February 1997	0.464	12.5	15.0	14.8	February
23 February 1997	0.532	14.5	16.6	14.8	February
11 March 1997	0.513	13.9	16.2	14.1	March
13 April 1997	0.540	14.7	16.8	13.0	April
29 April 1997	0.527	14.3	16.5	11.4	May
	South Chatham Rise			41°S	
25 June 1996	0.387	10.2	13.1	14.0	June
29 August 1996	0.320	8.3	11.5	13.0	August
30 September 1996	0.223	5.4	9.2	13.0	September
6 November 1996	0.224	5.4	9.2	14.7	November
4 December 1996	0.312	8.0	11.3	16.6	December
5 January 1997	0.363	9.5	12.5	18.0	January
7 February 199797	0.459	12.3	14.8	18.5	February
11 March 1997	0.573	15.7	17.6	18.0	March
13 April 1997	0.367	9.7	12.6	16.9	April

COADS are the monthly regional satellite temperatures for the closest grid point.

significant temperature deviations caused by eddies or other phenomena that could account for the temperatures recorded in the traps. $U^{K'}_{37}$ levels in the north trap recorded temperatures of 12–14 °C which were 4–6 °C cooler than actual temperatures from January to March of 1997. Weekly satellite reconstructions show that temperatures over that trap were warmer than average, being 15–19 °C throughout that period with warmer waters being delivered periodically by the Wairarapa Eddy. In contrast, the alkenone reconstructions in the south trap recorded temperatures in subantarctic waters that were warmer than regional monthly averages in late winter (August) and early autumn (March). Satellite real-time weekly averages in August 1996 and March 1997 were close to the COADS (1999) monthly averages with no evidence of the 3 °C warm anomaly seen in the trap record (see Fig. 2).

Current meters placed on the trap arrays allow us to estimate source areas for particles collected by the traps at 300 m depth, which suggests that particles were derived from within an area with a mean radius of 40 km for the northern trap site and 80 km for the southern trap (Nodder and Northcote, 2001). Directly over the Rise (rather than at the trap sites) there is a weak mean eastward geostrophic flow of 0.06 m s^{-1} (Chiswell, 1994a). Tidal flows of 0.11 m s^{-1} that are aligned zonally along the Rise, stir the water, resulting in resuspension of particles on the crest of the Rise At the southern site, the persistent eastward currents for most of the year-long deployment suggests that the particle source area is likely to

have been elongated parallel to the bathymetric contours and SST gradients that mark the southern side of the STF. At the northern site, currents are stronger and more variable and the particle source area is likely to be somewhat circular and elongated preferentially towards the west (Nodder and Northcote, 2001; unpublished current meter data). This evidence suggests limited north–south exchange across the Rise. Resuspension leads to local off-bank transport producing elevated mass fluxes in the deeper traps, which sit below the crest of the Rise (Nodder, 1997).

Sinking rates of particles for the Chatham Rise array are comparable to other deep ocean studies, with flux events in the 300 m traps echoed one cup later in the 1000 m traps on the same array suggesting a particle sinking rate of $\sim$100 m d^{-1} (King and Howard, 2001; Nodder and Northcote, 2001). While surface and deep traps from the same mooring reflect the same flux events, these events are uncorrelated with the opposite trap array (King and Howard, 2001; Nodder and Northcote, 2001), providing evidence against lateral transport of suspended or sinking particles across the Rise. Importantly, foraminiferal assemblages in the deeper traps show no measurable difference in their temperature signal from the shallow traps (King and Howard, 2001). While the STF exhibits significant mesoscale variability in circulation, the overall picture is well understood: the presence of a well defined, topographically anchored frontal system limits surface transport north–south across the Rise (Uddstrom and Oien, 1999). Lateral advection, mixing of particles and the transport of temperature signals across the Chatham Rise are likely to have a very limited effect on the interpretation of the sediment trap data.

3.2. Biomarker fluxes and distributions

3.2.1. North Chatham Rise, subtropical waters

Total long-chain alkenone fluxes for the north Chatham Rise ranged from 0.07 to 22.6 μg m^{-2} d^{-1} over the course of the deployment. Fluxes of the C_{37} alkenones ranged from 0.05–9.5 μg m^{-2} d^{-1}, with average fluxes being 2.6 μg m^{-2} d^{-1} (Table 2). These low fluxes are comparable to those observed in many mid-to high-latitude locations worldwide (e.g. the subtropical North Atlantic in winter; (Conte et al., 1998a) and non-monsoon times in the Arabian Sea (Prahl et al., 2001). There were four significant maxima in the measured fluxes during the course of our deployment: a minor one occurring in September, abating slightly before a major event in early October (late winter to early spring). A second major event occurred in mid-summer (early January). Frustratingly, the 5 cups prior to the January event were lost, so the exact timing of the start and full extent of this event are uncertain (Nodder and Northcote, 2001). The largest event had alkenone fluxes of 22.7 μg m^{-2} d^{-1} and occurred mid-summer (January, 1997). Measured fluxes in that event were five times the average flux for the deployment, approximately double that of the spring event (12.2 μg m^{-2} d^{-1}) and nearly three times the fluxes in the autumn event (8.5 μg m^{-2} d^{-1}) (Fig. 3a, Table 2). Our maximum fluxes are comparable to monsoon seasons in the Arabian Sea (Prahl et al., 2001) and as much as 5 times higher than maximum fluxes in less productive subtropical areas such as the Sargasso Sea (Conte et al., 1998b). This event was followed by a second smaller event in autumn (mid-March).

Total sterol fluxes and the fluxes of most of the individual marker sterols were very similar to the flux patterns of the alkenones in the subtropical trap (Fig. 3b). However, the timing and magnitude of dinosterol fluxes were substantially different. Maximum fluxes for all the other sterols occurred in January with the total sterol flux 7.8 mg m^{-2} d^{-1} (Table 2). Two smaller sterol flux maxima occurred during the deployment in September–October and March; these were also similar in relative magnitude and timing to the alkenone flux maxima. The late winter and spring flux events of the alkenones appear as one longer event with elevated fluxes in the first cup of the deployment, suggesting that for alkenones, the late winter event may have started before the deployment began, while fluxes in the other phytoplankton biomarker sterols generally increased through September to peak in the mid-October event. Elevated sterol fluxes lasted throughout September and early October (early spring) with total sterol fluxes ranging between 1.2 and 2.4 mg m^{-2} d^{-1} (Fig. 3a).

Table 2
Fluxes for alkenones and selected sterols discussed in the paper

Date trap opened	Absolute fluxes									Fluxes normalized to total fluxes							Fluxes normalized to POC						
	Total sterols	Ch	*T*-22	Br	24-Meth	Din	Alk	Total mass flux	POC	Total sterols	Ch	*T*-22	Br	24-Meth	Din	Alk	Total sterols	Ch	*T*-22	Br	24-Meth	Din	Alk
	Fluxes in $\mu g/m^2/day$							$(mg/m^2/d)$		µg/mg total flux					ng/mg	µg/mg	Fluxes in µg/mg POC flux						
North Chatham Rise																							
14-Sep-96	1257.2	630.9	122.5	100.6	81.5	0.0	4.31	110.3	6.4	11.4	5.7	110.3	0.9	0.7	0.00	39	195.2	98.0	19.0	15.6	12.7	0.0	0.669
22-Sep-96	2122.0	988.1	209.4	149.0	161.9	0.0	2.77	42.9	6.5	49.5	23.0	42.9	3.5	3.8	0.00	65	326.9	152.2	32.3	23.0	24.9	0.0	0.427
30-Sep-96	1448.9	677.3	189.8	68.9	80.3	0.0	2.23	74.4	22.2	19.5	9.1	74.4	0.9	1.1	0.00	30	65.2	30.5	8.5	3.1	3.6	0.0	0.100
08-Oct-96	2398.4	713.1	290.0	189.4	423.6	38.9	12.15	1064.9	141.7	2.3	0.7	1064.9	0.2	0.4	0.27	11	16.9	5.0	2.0	1.3	3.0	0.3	0.086
17-Oct-96	55.6	12.7	6.1	4.9	12.3	0.8	0.36	13.8	0.6	4.0	0.9	13.8	0.4	0.9	1.36	26	95.3	21.8	10.5	8.3	21.1	1.4	0.612
02-Nov-96	37.5	26.3	1.9	1.3	2.5	0.0	0.07	1.3	0.2	29.5	20.7	1.3	1.0	2.0	0.00	59	232.2	163.2	11.9	8.2	15.4	0.0	0.465
05-Jan-97	7870.7	1831.2	1525.4	1147.2	664.7	0.0	22.66	176.5	18.7	44.6	10.4	176.5	6.5	3.8	0.00	128	420.7	97.9	81.5	61.3	35.5	0.0	1.211
21-Jan-97	417.2	209.9	44.4	36.4	16.7	3.0	3.79	27.7	5.2	15.1	7.6	27.7	1.3	0.6	0.58	137	80.2	40.4	8.5	7.0	3.2	0.6	0.729
7-Feb-97	688.8	333.4	88.9	57.1	28.6	3.1	4.80	21.3	8.0	32.4	15.7	21.3	2.7	1.3	0.39	226	85.8	41.5	11.1	7.1	3.6	0.4	0.598
23-Feb-97	404.1	218.1	43.2	30.2	14.1	4.9	3.61	57.7	7.4	7.0	3.8	57.7	0.5	0.2	0.66	63	54.6	29.5	5.8	4.1	1.9	0.7	0.488
11-Mar-97	1106.8	619.5	128.0	72.1	42.8	7.6	8.55	124.4	13.3	8.9	5.0	124.4	0.6	0.3	0.57	69	83.1	46.5	9.6	5.4	3.2	0.6	0.642
13-Apr-97	82.0	36.8	9.3	8.0	3.8	1.2	1.70	18.2	2.9	4.5	2.0	18.2	0.4	0.2	0.40	93	28.1	12.6	3.2	2.8	1.3	0.4	0.584
29-Apr-97	10.0	3.1	1.5	0.9	0.3	0.2	0.19	2.4	0.1	4.1	1.3	2.4	0.4	0.1	1.63	77	103.1	32.2	15.4	9.8	3.5	1.6	1.924
South Chatham Rise																							
25-Jun-96	149.2	37.4	16.1	24.6	18.5	1.0	0.74	5.1	0.7	29.2	7.3	3.1	4.8	3.6	0.19	144	206.8	51.9	22.3	34.1	25.6	1.3	1.019
26-Jul-96	1817.7	1585.1	37.8	17.8	783.2	0.0	0.00	2.1	1.8	856.7	747.0	17.8	8.4	369.1	0.00	0	982.8	857.0	20.5	9.6	423.5	0.0	0.000
29-Aug-96	1423.0	229.7	145.3	285.6	113.5	14.0	16.83	48.4	9.6	29.4	4.7	3.0	5.9	2.3	0.29	348	148.1	23.9	15.1	29.7	11.8	1.5	1.752
30-Sep-96	2062.7	667.4	197.5	293.7	329.8	11.5	11.64	43.7	14.5	47.2	15.3	4.5	6.7	7.5	0.26	266	142.7	46.2	13.7	20.3	22.8	0.8	0.805
6-Nov-96	1034.2	185.2	300.2	112.7	91.5	29.5	21.83	288.7	14.8	3.6	0.6	1.0	0.4	0.3	0.10	76	70.0	12.5	20.3	7.6	6.2	2.0	1.479
4-Dec-96	520.4	132.0	99.3	85.7	65.2	2.1	8.20	9.1	10.8	57.1	14.5	10.9	9.4	7.2	0.23	899	48.0	12.2	9.2	7.9	6.0	0.2	0.756
5-Jan-97	13.9	3.7	1.2	2.0	1.8	0.5	0.21	0.3	0.2	43.6	11.5	3.7	6.4	5.7	1.67	659	80.0	21.1	6.9	11.7	10.4	3.1	1.210
7-Feb-97	1189.0	964.2	51.3	33.6	476.5	1.6	0.31	3.1	1.2	389.8	316.1	16.8	11.0	156.2	0.51	101	1029.1	834.6	44.4	29.1	412.4	1.3	0.267
11-Mar-97	830.3	330.9	108.5	73.1	163.5	2.2	0.14	3.2	0.6	261.1	104.1	34.1	23.0	51.4	0.71	44	1371.0	546.4	179.1	120.8	270.0	3.7	0.232
27-Mar-97	1575.2	821.5	74.9	170.2	405.9	1.3	0.00	6.4	1.5	247.7	129.2	11.8	26.8	63.8	0.20	0	1076.0	561.2	51.1	116.3	277.3	0.9	0.000
13-Apr-97	288.0	107.8	46.9	25.7	53.3	0.0	0.09	5.9	1.0	48.8	18.3	7.9	282.1	9.0	0.00	15	290.2	108.6	47.2	25.9	53.7	0.0	0.092

Note: Ch, Cholesterol; T-22, trans-22-dehydrocholesterol; Br, Brassicasterol; 24-Meth, 24-methylene-cholesterol; Din, Dinosterol; Alk, Alkenones.

Maximum sterol fluxes for the spring were about one-third the maximum of the summer event. The third and smallest lipid flux event occurred in March, with combined sterol fluxes of 1.1 mg m^{-2} d^{-1} which were slightly less than the average fluxes for the overall deployment of 1.4 mg m^{-2} d^{-1}. Individual sterol fluxes were highly variable and ranged between ~1 and 1800 μg m^{-2} d^{-1} between low flux and high flux events. Dinosterol fluxes were generally very low except for the high flux event of ~39 μg m^{-2} d^{-1} in October, which preceded by one cup the high fluxes seen in the other biomarkers. With the exception of this event, dinosterol was at, or below, detection limits in the spring and early summer, and reappeared at low concentrations in late summer and early autumn. Sterol fluxes averaged 100 times maximum fluxes in less productive areas such as NW Australia and Bermuda (Burns et al., 2003; Conte et al., 1998b).

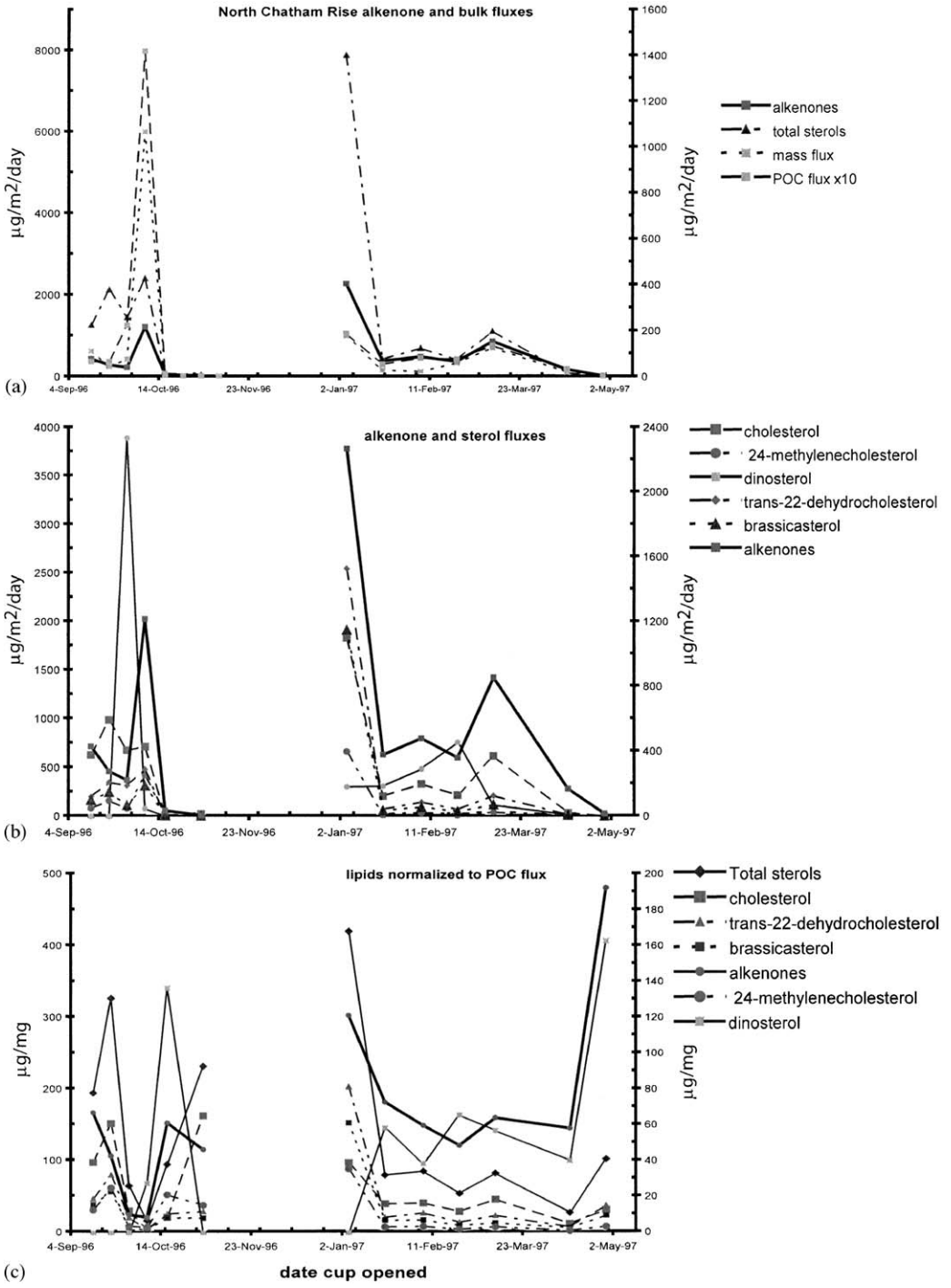
The total flux and POC flux showed a single dominant maximum flux event in early October (Nodder and Northcote, 2001) which contrasts with the pattern of several maxima in the lipid fluxes. Secondary, much smaller, maxima occurred in the bulk fluxes in January and March, but these were an order of magnitude less than during the event in October. Thus, when sterol and alkenone fluxes are normalized to POC their patterns differ quite noticeably from the fluxes seen in the bulk parameters and with each other (Fig. 3c).

All sterols and alkenones made up a much smaller proportion of overall organic flux in the spring (October) event than in the summer (January) event, with biomarker fluxes in the spring flux event being the lowest of the entire deployment when expressed as a proportion of the bulk parameters. In contrast, despite the high fluxes of alkenones and sterols associated with that event, these lipids were a very small part of the organic flux in the spring bloom and relatively large proportion of the organic flux during the summer event (Fig. 3c). The proportion of alkenones relative to total flux and POC was highest during and right after the summer event (Fig. 2a). This mid-summer event coincides with the period when the temperature reconstructions deviate the most from the satellite SST. Alkenones relative to POC flux were highest late in the deployment during early autumn. Fluxes of the several diatom biomarker sterols generally paralleled one another and the alkenones through the deployment, with epi-brassicasterol (a sterol also made by alkenone producers) being relatively more abundant when the alkenone fluxes were highest (Table 2). Cholesterol, considered a zooplankton marker, showed fluxes that generally paralleled those of the other lipids, with the exception that cholesterol fluxes were relatively elevated in the late winter immediately preceding the spring bloom. Overall, cholesterol made up a smaller percentage (~23% of the total sterols) of the sterol flux when fluxes were high and a much larger percentage (70%) when fluxes were lowest (Fig. 3, Table 2).

3.3. South Chatham Rise, subantarctic waters

Total alkenone fluxes for the south Chatham Rise in 1996–1997 had a maximum and minimum range similar to that at the north Chatham Rise site (0.09–21.8 μg m^{-2} d^{-1}) (Table 2). However, unlike subtropical waters, high alkenone fluxes in the subantarctic waters occurred as one prolonged event beginning in August (late winter), peaking in November (late spring), and ending in December (early summer). This flux pattern is also broadly reflected in the fluxes of the biomarker sterols and total mass and POC fluxes for the duration of the deployment (Nodder and Northcote, 2001). Alkenone fluxes before and after the main flux event are less than 1 μg m^{-2} d^{-1} (0.09–0.74 μg m^{-2} d^{-1}) and during the event they are 1–2 orders of magnitude higher (8–21 μg m^{-2} d^{-1}) (Table 2). The alkenone fluxes during the spring event tended to lag changes in POC and sterols by one cup (16 d), and peaked at the same time as total mass flux in early November (Fig. 4a).

Total sterol fluxes varied from ~0.015–0.02 mg m^{-2} d^{-1} except for very low fluxes in January of ~13 μg m^{-2} d^{-1}. The overall sterol fluxes generally mimicked changes in POC flux more closely than total mass or alkenone flux, showing a broad increase through the spring and a second smaller increase in fluxes in the autumn when alkenone fluxes showed little change


North Chatham Rise alkenone and bulk fluxes
µg/m2/day
µg/m2/day
alkenones
total sterols
mass flux
POC flux x10
4-Sep-96
14-Oct-96
23-Nov-96
2-Jan-97
11-Feb-97
23-Mar-97
2-May-97
(a)
alkenone and sterol fluxes
µg/m2/day
µg/m2/day
cholesterol
24-methylenecholesterol
dinosterol
trans-22-dehydrocholesterol
brassicasterol
alkenones
(b)
lipids normalized to POC flux
µg/mg
µg/mg
Total sterols
cholesterol
trans-22-dehydrocholesterol
brassicasterol
alkenones
24-methylenecholesterol
dinosterol
(c)
date cup opened

(Fig. 4b). The biomarker sterols generally followed this pattern, with fluxes varying from ~1 to 1500 $\mu g\,m^{-2}\,d^{-1}$ (Table 2). One exception was the data for cholesterol, which had peak fluxes in July, one cup before the increase in the diatom marker sterols, after which cholesterol fluxes dropped with the onset of the spring bloom event and remained relatively low throughout the bloom. In autumn, cholesterol fluxes rose in concert with the other sterols.

The four sterols chosen as phytoplankton indicators all showed increases in flux coincident with the increase in POC flux, but the peak flux of individual compounds showed a temporal succession. Epi-brassicasterol fluxes rose most rapidly and reached peak values in late August to early September, whereas the 24-methylenecholesterol fluxes peaked in late September to early October. The flux of *trans*-22-dehydrocholesterol peaked in early November, coincident with both the dinosterol and alkenone fluxes and the spike in POC flux. All sterol fluxes then dropped rapidly through December along with the POC fluxes. However, the reduction in lipid fluxes was more gradual than that seen in total fluxes (Fig. 4a). The fluxes of diatom sterols and cholesterol then began to increase through February and March. Again, cholesterol fluxes reached a peak first, early in February, after which levels fell off, but not so dramatically as in the spring, after which the phytoplankton marker sterols increased. Unlike the spring, the *trans*-22-dehydrocholesterol fluxes peaked next followed by the other diatom sterols, 24-methylenecholesterol and epi-brassicasterol, while neither alkenones nor dinosterol showed any autumnal increase in flux (Fig. 4b). This lack of correlation between sterols and alkenones in autumn provides clear evidence that the epi-brassicasterol here is mostly derived from diatoms and not haptophytes.

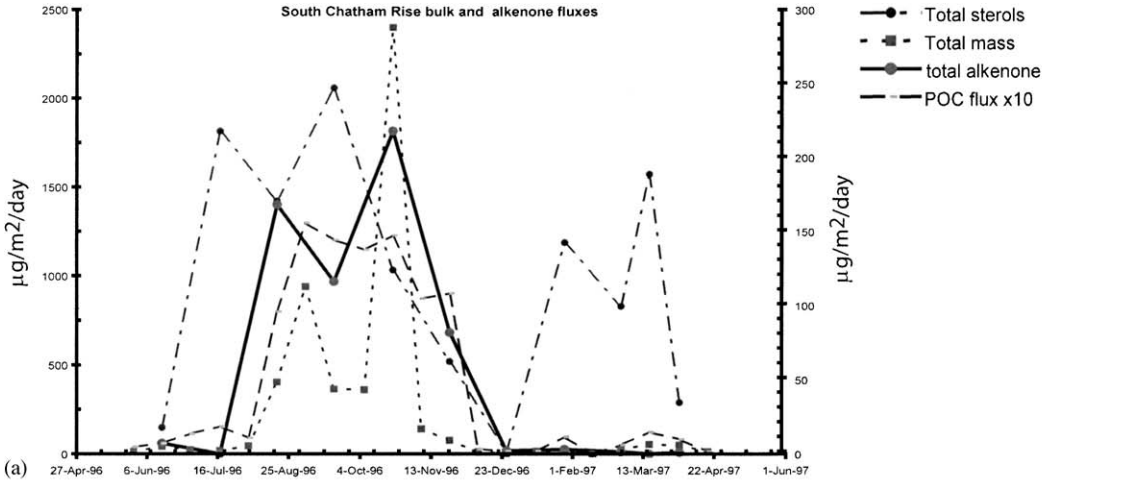
As in subtropical waters, when biomarker fluxes are normalized to POC fluxes in subantarctic waters the relative distributions look quite different. Although absolute fluxes for all biomarkers were highest in the spring, alkenone fluxes normalized to POC were low in the spring, and relatively higher in the summer, returning to low levels as a proportion of the total organic flux in the autumn (Fig. 4c). In contrast, the fluxes of individual sterols normalized to POC were relatively low from early spring to summer (August through January) after being a high proportion of the flux in late winter to early spring (July). Alkenone fluxes normalized to POC were completely out of phase with the flux of marker sterols and represented a higher proportion of the total organics when the sterol contents were low.

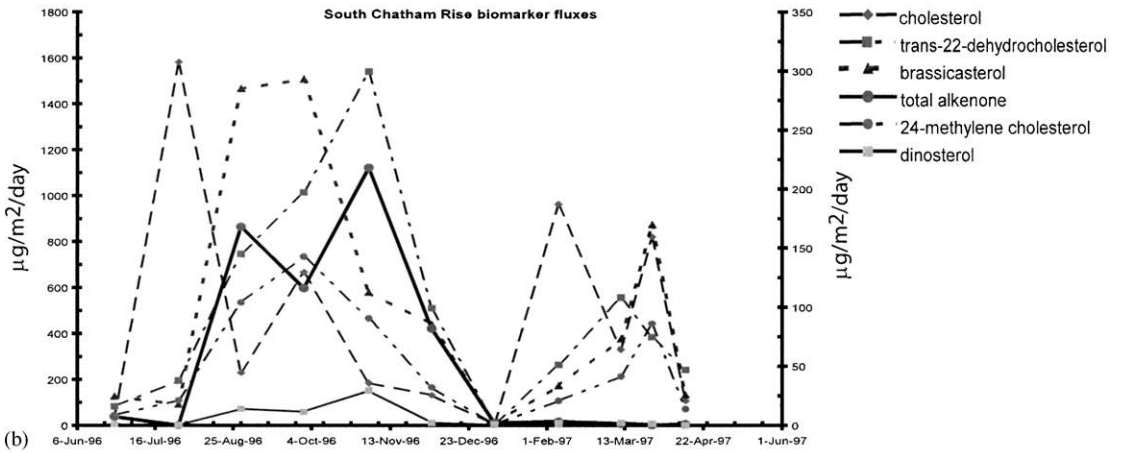
4. Discussion

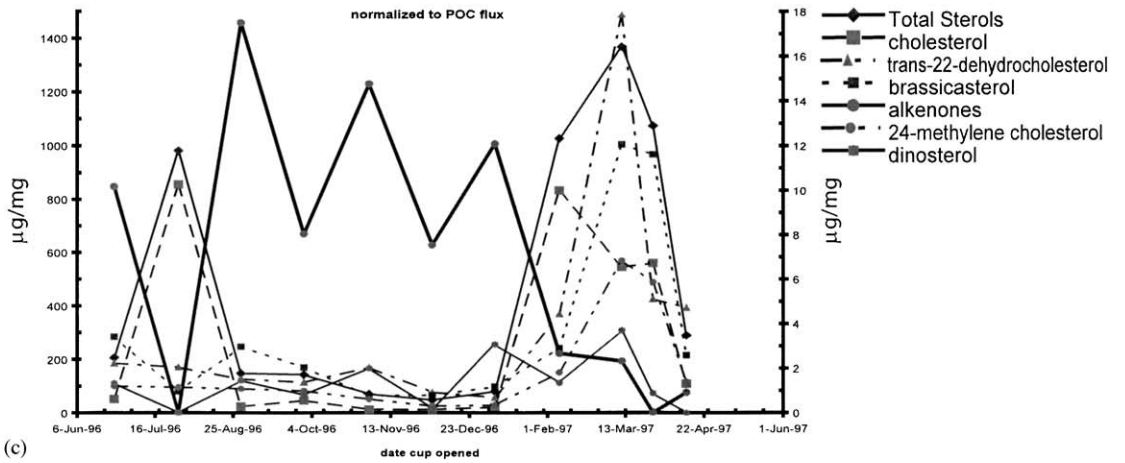
4.1. Temperatures

Comparison of temperatures from real-time satellite SST records and alkenone SST reconstructions clearly demonstrates that the alkenones reproduce SST for the majority of the deployment, but they do not record actual SST at all times. Although these are the minority of the year, we examine these times with anamolous SST reconstructions in more detail for clues about controls on alkenone unsaturation levels. The weekly satellite data for the duration of the deployments show several ~1 °C deviations to warmer temperatures from the long-term averages in subtropical waters whereas alkenone reconstructions are up to 4 °C cooler. In the subantarctic locality the situation is reversed. Therefore, these temperature deviations in our trap record must be due to environmental factors known to affect alkenone

Fig. 3. Fluxes for biomarker lipids and bulk parameters for the subtropical (northern) trap: (a) Absolute fluxes for alkenones, total sterols and the bulk parameters total mass flux and particulate organic flux (POC). (b). Absolute fluxes for alkenones and selected sterols. (c) Fluxes for alkenones and biomarker sterols normalized to particulate organic carbon (POC). Normalizing the fluxes of the individual lipids to POC illustrates how the flux of individual compounds varies as a proportion of the organic flux. Alkenone fluxes are high in October during the spring bloom, when fluxes of all parameters are high. However, alkenone and sterol fluxes are highest in January, when POC fluxes are low. Thus, alkenones are a greater proportion of the organic flux in the late summer and early autumn than in the spring.


South Chatham Rise bulk and alkenone fluxes
µg/m2/day
µg/m2/day
Total sterols
Total mass
total alkenone
POC flux x10
(a)
27-Apr-96
6-Jun-96
16-Jul-96
25-Aug-96
4-Oct-96
13-Nov-96
23-Dec-96
1-Feb-97
13-Mar-97
22-Apr-97
1-Jun-97


South Chatham Rise biomarker fluxes
µg/m2/day
µg/m2/day
cholesterol
trans-22-dehydrocholesterol
brassicasterol
total alkenone
24-methylene cholesterol
dinosterol
(b)
6-Jun-96
16-Jul-96
25-Aug-96
4-Oct-96
13-Nov-96
23-Dec-96
1-Feb-97
13-Mar-97
22-Apr-97
1-Jun-97

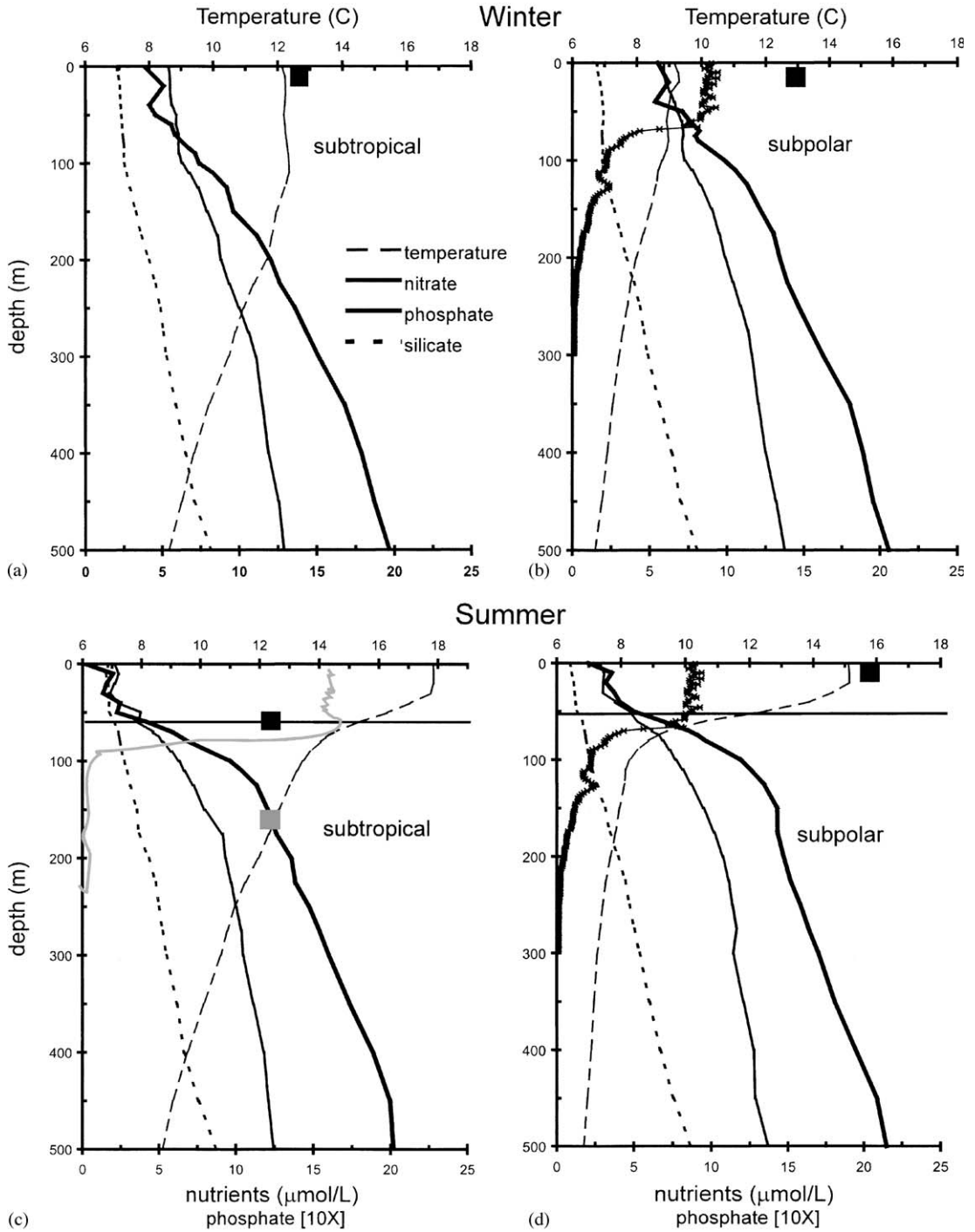

normalized to POC flux
µg/mg
µg/mg
Total Sterols
cholesterol
trans-22-dehydrocholesterol
brassicasterol
alkenones
24-methylene cholesterol
dinosterol
(c)
6-Jun-96
16-Jul-96
25-Aug-96
4-Oct-96
13-Nov-96
23-Dec-96
1-Feb-97
13-Mar-97
22-Apr-97
1-Jun-97
date cup opened

distributions such as nutrients, light levels or other stresses (Conte et al., 1998a; Epstein et al., 2001, 1998b; Herbert, 2001; Laws et al., 2001; Popp et al., 1998; Prahl et al., 2000a, 2003; Versteegh et al., 2001).

We can assess the potential influence of nutrients on alkenone production at the trap sites. Compiled profiles of nutrients and temperature for the trap sites are available from the CSIRO Atlas of Regional Seas (CARS: Ridgway et al., 2002). This composite provides a detailed picture of the average nutrient and thermocline profiles in the location of the traps (Fig. 5). Multiple CTD and bottle casts from the trap locations, taken between 1991 and 1999 agree well with the atlas values (S. Nodder, NIWA unpublished data). Nutrient distributions in this location show annual variations typical of open mid-latitude oceanic locations. Nutrient levels are high in the surface mixed layer in the winter (July–August) when the thermocline is deep or missing, and lower in mid-summer (January) when the thermocline is very well established in both water masses at ~40 m (Fig. 5). Hydrocast data averaged from several casts in the location of the traps in January indicate that that on average, in both water masses, surface nutrients are only moderately low in summer (~3 μM nitrate and ~0.3 μM phosphate; in subtropical waters and ~4 μM nitrate and ~0.4 μM phosphate in subantarctic waters), and fluorescence (a proxy for total chlorophyll levels) is elevated through the mixed-layer and can exhibit a slight maximum at the base (Fig. 5) (Ridgway et al., 2002). Significantly, the low nutrient concentrations present in the surface mixed layer in subtropical waters dip below the levels at which culture work indicates nutrient stress effects occur in *E. huxleyi* (i.e. ~4 μM nitrate and ~0.2 μM phosphate; Prahl et al., 2003). Nutrient levels in the surface mixed layer of the subpolar waters do not drop below these threshold values (Fig. 5b and d). In our subtropical traps, alkenone temperature reconstructions were too cool at two times during mid and late summer, when alkenone export production was highest in absolute terms and also highest relative to POC flux (Fig. 3c). These anomalously cool alkenone SST reconstructions occurred when the thermocline was well established and nutrient levels fell below the levels shown to affect alkenone unsaturation levels in cultures (Prahl et al., 2003).

In the January high flux event, alkenones recorded temperatures of 12 °C. We interpret these lowered temperatures as likely to be due in part to nutrient stress effects of the type seen in the culture experiments of Prahl et al. (2003), because in January the depth in the water column at which the temperature reaches 12 °C is approximately 200 m (Fig. 5c), well below the depth of the marked decline in fluorescence which is consistently associated with the base of the thermocline regionally (Ridgway et al., 2002). There is also likely to be some production at the base of the mixed layer (where temperatures drop by 1–2 °C and fluorescence remains high), but it is significant that nutrients in January drop to levels shown in the laboratory to activate the biosynthesis mechanisms that reduce alkenone unsaturation levels. We cannot directly assess nutrient levels for January 1997 with the data available. However, the hydrocast data indicate that for the alkenones to be faithfully recording 12 °C temperature due to subsurface production alone, the majority of them must be produced at nearly 200 m depth, which is not supported by the fluorescence data. Results from the oligotrophic north Pacific (Popp and Prahl, 2001; Prahl et al., 1993) suggest that when haptophytes grow in the surface mixed layer under nutrient stress, their alkenones record temperatures up to 2 °C cooler than ambient. The effect seen in our traps might then be a combination

Fig. 4. Fluxes for lipid biomarkers and bulk parameters for the subantarctic (southern) trap location: (a) Absolute fluxes for alkenones, total sterols and the bulk parameters total mass flux and particulate organic flux (POC). (b) Absolute fluxes for alkenones and selected sterols. (c) Fluxes for alkenones and biomarker sterols normalized to particulate organic carbon (POC). Normalizing the fluxes of the individual lipids to POC illustrates how the flux of individual compounds varies as a proportion of the organic flux. Alkenone fluxes are high in later winter–early spring, along with bulk fluxes and other biomarkers, but unlike the others, alkenone fluxes do not increase in late summer. Alkenone fluxes normalized to POC fluxes show opposite trends to all other biomarker compounds (panel c) indicating a different response to environmental conditions than these other markers.


Winter
Temperature (C)
Temperature (C)
subtropical
subpolar
temperature
nitrate
phosphate
'silicate
depth (m)
(a)
(b)
Summer
subtropical
subpolar
depth (m)
nutrients (μmol/L)
phosphate [10X]
nutrients (μmol/L)
phosphate [10X]
(c)
(d)

of factors, but a physiological response must be part of the signal.

In January, 1997 on the north Chatham Rise, the full measure of cool temperatures cannot have been caused solely by production at depth, with physiological factors responsible for at least 2 °C of the temperature reduction. The second "low" $U^{K'}_{37}$ temperature event in subtropical waters occurred during the extended moderate fluxes event through March 1997. Ambient surface mixed layer temperatures in March were 16–18 °C and shallowing of the thermocline brought the 14 °C isotherm to within 60–80 m of the surface, within the photic zone but with lowered light levels (Fig. 5c). Thus, conceivably the alkenone producers could be growing at the base of the mixed-layer in March and recording the ambient temperature there (as supported by the fluorescence data which suggests high productivity at the base of the mixed layer; Ridgway et al., 2002). However, our results support previous work suggesting a combination of physiological factors contribute to the anomalous temperatures, providing clear evidence that production below or at the base of the thermocline "in calibration" with ambient temperatures cannot be the only cause of "too cool" proxy temperatures recorded in sediment trap samples.

In contrast to the subtropical site, our trap results from subpolar (high nutrient) waters show only warm temperature anomalies, which is the opposite of that found in nearby subtropical waters. Temperatures in July to early September and again in March (14 and 18 °C, respectively) were ~4 °C higher than the weekly satellite temperatures (10 and 14 °C, respectively). These "too warm" temperature excursions are associated with low fluxes both in winter (no stratification) and in early fall (maximum stratification) (Fig. 5 b and d), whereas alkenone-derived temperatures generally reflected SST values when alkenone fluxes were high in absolute terms and relative to POC fluxes (Fig. 4c). Hydrocast data from the trap location show that nutrient levels (~4 μM nitrate and ~0.5 μM phosphate; Ridgway et al., 2002) are higher than the approximate "threshold" values in cultures for the onset of physiological effects on $U^{K'}_{37}$ even in late summer to early autumn (Fig. 5). Too-warm temperatures from the alkenones cannot logically be ascribed to growth of the microalgae deep in the water column, pointing to some combination of ecological factors as the cause.

Using the laboratory results of Prahl et al. (2003) as a model we can postulate that the warm temperatures reflect the physiological effects of slow growth under low light levels or trophic stress. Weekly composites of regional satellite ocean color data confirm that moderate chlorophyll levels were patchy and present from January throughout the autumn of 1997 (0.5–1.0 mg m^{-3}). These data suggest that the autumn bloom of phytoplankton, which had low levels of alkenones, may have been occurring deep in the water

Fig. 5. Average nutrient profiles of nitrate and phosphate plotted with temperature for the location of the sediment traps. Northern location is 42°42′S 178°38′E; southern trap location is 44°37′S 178°37′E. representative profiles for: (a) subtropical winter (August); (b) subpolar winter (August); (c) late subtropical summer (March); (d) late subpolar summer (March). Nutrient and temperature values in the plots are for a given date, but are representative of seasonal values for the location and agree well with actual hydrocast data from the location of the traps. In all panels: solid thick black line is nitrate data, thin black line is phosphate data, dashed line is temperature data, dotted line is silicate data. Black squares indicate = 0.0414T—0.156 the temperature recorded by alkenones for that location and season. Horizontal lines in panels c and d indicate the approximate location of the thermocline. In panels b and d, the thin line with symbols is fluorescence data from a single hydrocast taken near the trap site during the season indicated; in panel c the gray line is fluorescence data from a single hydrocast taken at the latitude of the trap site, but several degrees of latitude to the east. Fluorescence levels are considered to indicate total productivity not just that of alkenone producers and are presented in arbitrary units not plotted to scale. Note that for both seasons in subpolar waters, elevated levels of fluorescence extend to depths at which nutrient levels begin to increase. Panel c illustrates that in subtropical summer, when alkenone fluxes were highest, the alkenones record a temperature that was present at a depth of ~200 m (gray square). Panel b illustrates that alkenone reconstructions were warmer than the temperatures present in summer, and high levels of productivity at and below the thermocline suggest that some of that productivity was occurring in low light conditions. It must be noted, however, that alkenone fluxes were very low during this period. For all other times, the alkenone temperature reconstructions agree with surface mixed layer temperatures at the trap locations.

column, which would have imposed light limitations on the alkenone producers. Fluorescence levels from local area hydrocasts are high in the top 100 m but cannot uniquely assess the location of alkenone production because alkenone producers are only a small to moderate portion of the biomass in these waters (Bradford-Grieve et al., 1997; Chang and Gall, 1998). Of the three cups that returned anomalous temperatures in the subantarctic trap only one (early September) has any appreciable flux, suggesting that the alkenone producers were either not growing rapidly or producing few alkenones under these conditions. A similar phenomenon was also seen in trap data from the Arabian Sea during the latter part of upwelling events (Prahl et al., 2000b). There, alkenone temperature reconstructions were warmer than actual SST at times when alkenone fluxes were relatively low and a low proportion of the organic flux, or biomarkers indicate that at least one other phytoplankton species was growing more rapidly. In our traps, the timing of the normalized fluxes show the alkenone fluxes rising after the diatom markers, and the relative importance of alkenone fluxes when diatom associated markers are low indicate that the alkenone export production is low when export of the diatom markers is high. Thus, in these two nutrient-rich environments, when the alkenone-producing haptophytes are out-competed they produce the same signal as laboratory cultures of *E. huxleyi* that are under stress. The dynamics controlling overall alkenone patterns in the high nutrient low chlorophyll (HNLC) waters of the Southern Ocean, where light limitation has been shown to be a factor in some seasons (Boyd et al., 1999), appear to be very different from those in nearby subtropical waters to the north.

These temperature variations are important for paleotemperature applications, especially when flux-weighted values are considered. During 1996–1997 in subtropical waters, the flux-weighted average alkenone SST was 14 °C, which is 1.5 °C cooler than COADS annual averages (15.5 °C). Alkenone distributions that matched surface mixed-layer temperatures were only ~20% of the alkenone flux, for the year. The early January event was responsible for nearly 40% of the annual flux, and the extended moderate fluxes that lasted from late January to March were also responsible for nearly 40% of the annual flux. If the production occurred exclusively at the base of the mixed layer through late summer and early autumn, then a maximum of 15% of the signal could be ascribed to alkenone synthesis that occurred in calibration with the water temperatures in which the phytoplankton grew. However, physiological effects are likely to have been a contributing factor to lowered inferred temperatures through the summer and autumn, suggesting that as much as 80% of alkenone production in 1996–1997 had unsaturation levels that differed from standard calibrations, making alkenone temperatures for the year dominated by "non-calibration" production. This observation strongly suggests that the alkenone temperature record in the sediments will be biased by these factors as well, and that these factors should be considered along with lateral transport (Benthien and Müller, 2000) when sedimentary temperature proxy records, particularly multi-proxy records, are considered.

In contrast, alkenone temperature reconstructions in subantarctic waters closely matched SST values at times when alkenone fluxes to sediments were greatest. This has significant implications for alkenone temperature paleo-reconstructions in subantarctic locations in contrast with subtropical waters. The spring bloom in 1996 was responsible for 97% of the alkenone flux out of the mixed-layer in 1996–1997, and most of the alkenones produced in that bloom (or 70% of the flux for the whole deployment) had the distributions expected for the observed surface mixed-layer temperatures. Alkenones produced in the earliest part of the spring bloom had temperatures just 2 °C warmer than ambient, and were responsible for only ~28% of the total alkenone flux. The fact that the bulk of the alkenones transported out of the surface waters reflects the temperatures of the surface mixed layer means that the season of alkenone production will dominate the alkenone temperature record in the sediments. This is reflected in the fact that the flux-weighted average temperature of 11 °C is only 0.5 °C cooler than the annual average COADS temperature of 11.5 °C for this location. The warm bias of the alkenones in Subantarctic waters, as well as the low contribution of alkenones with biased tempera-

tures to the flux, are both opposite the pattern found in subtropical waters. This observation suggests that the $U^{K'}_{37}$ record of temperature found in Subantarctic sediments will better reflect the temperature of the waters in which the phytoplankton grew (or they will show a small bias to warmer values), which contrasts sharply to our findings for subtropical waters. This conclusion may be significant in understanding the inferred temperature offsets found between alkenones and foraminifera in glacial age sediments south of the Chatham Rise. Foraminiferal reconstructions indicate that glacial SST was 4 °C cooler than alkenones, which our results suggest may have both a seasonal and physiological component (Sikes et al., 2002).

Previous sediment trap work and water column studies have suggested that "too cool" temperature reconstructions may be due to subsurface production (Harada et al., 2001; Prahl et al., 1993; Ternois et al., 1997), whereas culture studies have implicated growth rates, nutrients, and light levels as having an effect on alkenone distributions (Epstein et al., 1998b; Versteegh et al., 2001). Our trap results are among the first field data to confirm that subsurface production alone cannot be the cause of the temperature deviations observed in alkenone fluxes out of the mixed layer, which will ultimately determine the signal in the sediments. This supports the results of Prahl et al. (2003), who found that nutrient stress decreases alkenone unsaturation levels and light stress increases them. This also suggests that "too cool" $U^{K'}_{37}$ values found in sediments can be due to physiological factors rather than being caused by lateral transport from cooler locations (Benthien and Müller, 2000).

4.2. Temporal patterns of biomarker flux

The C_{37} alkenones serve as ideal biomarkers for a limited number of haptophytes. In this region of the open ocean the only known alkenone producers are the closely related species *G. oceanica* and *E. huxleyi*. Therefore, the presence of alkenones almost certainly indicates the presence of one or both of these two species and the fluxes can be interpreted as indicating relative changes in their export production. In contrast, a great diversity of sterols are found in microalgae and in particular, many diatoms synthesize a suite of sterols (e.g. Barrett et al., 1995). Both haptophytes contain epi-brassicasterol as the only major sterol and the interpretation of the proportion of alkenones to epi-brassicasterol can be complicated somewhat by the fact that the relative levels of alkenones per cell have been shown to vary widely (e.g. Epstein et al., 2001; Prahl et al., 2003) and the relative variation in levels of alkenones to epi-brassicasterol is not known. Thus, some caution is needed when epi-brassicasterol is used as a diatom marker; the related sterol 24-methylenecholesterol can be used more confidently as a proxy for diatom production. Cholesterol is often taken as evidence for zooplankton (either as body parts or as fecal material), although some contribution from microalgae is also possible (Volkman et al., 1986).

4.3. Subtropics

In subtropical waters, cholesterol fluxes showed significant changes relative to the phytoplankton lipids throughout the deployment, reflecting changes over the seasonal cycle in the proportions of zooplankton to phytoplankton in surface waters. In winter, cholesterol fluxes were relatively high, suggesting that grazers were dominating export production. In winter, grazing by microzooplankton can account for 100% of production in this area (James and Hall, 1998), but most of this material is recycled in the upper water layers and not exported to depth. Cholesterol represents almost half of the sterol flux throughout most of the deployment except during the high phytoplankton flux events in the spring and summer, when it drops to about a fifth of the total sterols. The spring flux maximum in lipids began in late September and was short lived (1–2 weeks) ending by mid-October (Fig. 3c). Cholesterol amounts increased relative to phytoplankton lipids in the cup that followed the highest overall fluxes, showing a typically delayed response of grazers to a phytoplankton bloom (e.g. Parsons et al., 1977). A similar response is also seen in increased bacterial and mesozooplankton biomass as well as pigment fluxes on the Chatham Rise following the

spring bloom (Bradford-Grieve et al., 1998; Nodder and Gall, 1998). The contribution from grazers becomes a relatively smaller proportion of the flux in these short-lived blooms, despite the fact that absolute cholesterol fluxes increased along with the other lipids. After the high-flux event in January and continuing through the autumn, cholesterol fluxes remained high relative to phytoplankton markers. This is entirely consistent with the important role played by fecal pellets in the accelerated and increased flux of less degraded material (Nodder and Gall, 1998) and the higher proportion of lipids to POC flux at that time.

The main spring high-flux event for lipids coincided with the single large pulse in total mass flux, POC (Fig. 3a), and biogenic silica ($\sim$6 mg m^{-2} d^{-1}), which was an order of magnitude higher than that seen in these bulk fluxes during the remainder of the year (Nodder and Northcote, 2001). Although the cups from mid-November to January were lost from the 300 m trap, analyses of bulk fluxes from the deeper trap confirm that bulk fluxes remained low in November–January (Nodder and Northcote, 2001). Unlike the spring event, the January (mid-summer) flux event was expressed only in the higher lipid fluxes, and not reflected in elevated mass, POC or silica fluxes (which were only $\sim$0.03 mg m^{-2} d^{-1}). This suggests that the spring event was characterized by export from siliceous organisms and that the flux was dominated by the sinking of their tests. In contrast, the bulk fluxes were a relatively small proportion of the January event, which had proportionally larger lipid biomarker fluxes. The proportion of phytoplankton lipids and alkenones in particular, rose relative to cholesterol and the bulk parameters (POC, biogenic silica). High alkenone contents may reflect the fact that the microalgae were laying down lipid reserves as nitrogen levels in the seawater dropped. Nutrient-starved cells have been shown to accumulate more than three times the concentration of alkenones than cells growing with ample nutrients (Prahl et al., 2003). This may indicate that alkenones and sterols were a higher proportion of biomass as well as export production. A high proportion of characterizable lipids to POC may indicate that particles that were sinking in that event were less degraded than in the organic matter sedimenting at other times of the year (Wakeham et al., 1997).

Of the biomarker lipids in subtropical waters, only dinosterol had a significantly different flux pattern. Dinosterol fluxes rose earlier and more quickly in the spring and pulsed before the major flux event. Only dinosterol had greatest fluxes in the spring bloom, and it showed an increase in proportion to POC (total organic flux) when all other lipid fluxes dropped in proportion to bulk fluxes indicating a significant increase in export production of dinoflagellates in the spring bloom (Fig. 3a and b). Nonetheless, dinosterol was always a minor component of the sterol fractions, indicating that dinoflagellate export production was a minor portion of the overall phytoplankton export in both subtropical and subpolar waters (Table 2; note difference in scale for dinosterol in Fig. 3a and b).

In subtropical waters, there was no appreciable sequence or significant change in the relative dominance among the phytoplankton biomarkers with the exception of dinosterol. These marker sterols pulsed simultaneously and remained in similar proportions throughout the trap deployment. Alkenone fluxes kept pace with, and responded similarly to, the conditions that sparked the bloom in diatoms, which we interpret as indicating that the source organisms remained in relatively the same proportion throughout the growth season in 1996–1997. However, because export production is estimated to be 2–4% of primary production (Nodder and Northcote, 2001), mechanisms that cause organic matter to sink out of the mixed layer can confound the signal. Alternatively, flux out of the surface mixed layer may be enhanced by zooplankton grazing, and organisms contributing to the flux may have selectively fed on the same microalgae throughout the deployment, with other species not being grazed to the same extent.

4.4. Subantarctic

The spring bloom in the subantarctic waters, as indicated by POC fluxes, occurred over a period of

4 months (Nodder and Northcote, 2001) (Fig. 4a). In contrast to subtropical waters, the bloom begins in late August, over a month before the subtropical bloom. Total mass and biogenic silica fluxes peak in mid November, and elevated fluxes last until mid-December, remaining elevated six weeks later than the end of the subtropical bloom. As the spring bloom evolved in subpolar waters, the phytoplankton biomarker fluxes showed a clear sequence of increasing fluxes, indicating a succession in phytoplankton species in the spring bloom. Epi-brassicasterol and 24-methylenecholesterol peaked earlier than alkenones and dinosterol suggesting that diatoms pulse early (albeit slightly) in the event (Volkman et al., 1998). Other diatoms (represented by *trans*-22-dehydrocholesterol), haptophytes, and dinoflagellates increase later in the bloom; Fig. 4b). This may be because seasonal grazing rate increases in subantarctic waters are 4–8 times less than the increases seen in subtropical waters in this area (Bradford-Grieve et al., 1998). After the broad spring bloom, subpolar fluxes of all lipids were negligible in January and remained low in February, after which most biomarkers showed a second flux event in March (autumn). Lipid fluxes in this "autumn bloom" are about one-half to one-third those seen in the spring, with *trans*-22-dehydrocholesterol increasing earlier in this event, suggesting that some diatoms were outpaced in this productivity pulse, with other diatom species peaking earlier. Neither alkenones nor dinosterol show an autumn increase, indicating that the coccolithophores and the dinoflagellates did not respond to the conditions that caused the diatom populations to increase. It remains possible that they bloomed after the traps were collected in May. In both events, the sequence of lipid fluxes suggests that in subantarctic waters, where nutrient concentrations are relatively high at the onset of the blooms (Bradford-Grieve et al., 1997), the haptophytes and dinoflagellates appear to be out-competed by the larger diatoms in bloom situations. This observation is consistent with the known ability of diatoms to take up nutrients more efficiently than the haptophytes and to out-compete them in situations where nutrients are abundant, leaving the smaller phytoplankton to bloom after nutrient concentrations drop (e.g. Mitchell-Innes and Winter, 1987; Ziveri and Thunell, 2000).

As in subtropical waters, cholesterol fluxes are high ($\sim$1500 $\mu g\,m^{-2}\,d^{-1}$) in the late winter and cholesterol is over 80% of the sterols present, suggesting grazers were prevalent prior to the spring bloom (James and Hall, 1998). During the extended phytoplankton bloom from August to November, cholesterol fluxes relative to other lipids were reduced and remained low (about one-fifth of the total sterols). Following the crash of the spring export event, cholesterol fluxes rebounded ahead of other lipids ($\sim$960 $\mu g\,m^{-2}\,d^{-1}$), increasing to become over 80% of the sterols present. They remained $\sim$30–50% of the total sterols, which may indicate a higher proportion of grazer contribution to the autumn bloom flux than in the spring. This differs from the subtropical autumn flux event. The higher proportions of grazer biomarkers and the more rapid response of these organisms to the smaller autumn bloom may be due to the very different zooplankton populations present in the two water masses in this area (Bradford-Grieve et al., 1998).

The temporal changes in POC fluxes are noticeably different to the biomarker fluxes during the subantarctic deployment (Fig. 4c). When biomarker fluxes are normalized to the POC flux, these data highlight the differences in interspecies dynamics between the two water masses and in particular between calcareous (alkenone producers) and siliceous (diatom) primary producers. In the subtropical site, biomarker sterol and alkenones fluxes behave similarly; they were a low proportion of the spring bloom when biogenic silica and particulate organic fluxes were high, and were a relatively higher proportion of the organic flux throughout the rest of the deployment. In contrast, the relative proportion of alkenones to the sterol biomarker fluxes were completely out of phase at the subantarctic site. In subpolar waters, the zooplankton marker sterol (cholesterol) flux was most important prior to the spring bloom; alkenone fluxes were relatively more abundant late in the spring, remained high through the summer, and then dropped at the onset of the fall bloom, when the diatom biomarkers were most dominant (Fig. 4c). The alkenone subantarctic distributions

contrast strongly with the subtropical waters where their proportion of the organic flux is relatively fixed through both the spring and fall blooms (Fig. 3c). Because alkenones act in part as storage lipids, and are preferentially produced when nutrients are low (Prahl et al., 2003), the relatively higher summer fluxes suggest there may have been some nutrient stress (due to temporary stratification?) in subantarctic waters in the summer of 1996–1997.

5. Conclusions

Alkenone and biomarker sterol fluxes in closely situated sediment traps deployed on the Chatham Rise east of New Zealand in 1996–1997 showed distinctly different temporal variation in subtropical waters compared with subantarctic waters. $U^{K'}_{37}$ temperature reconstructions, based on the Sikes and Volkman (1993) calibration largely reflected surface mixed layer temperatures in both water masses. However, there were times when alkenone-based temperature reconstructions showed significant deviations from SST as estimated from satellite observations. We have examined these times in detail to get a better understanding non-thermal controls on alkenone unsaturation.

$U^{K'}_{37}$ temperature reconstructions in subtropical waters showed biases of up to 4 °C towards cooler values in concert with rapid phytoplankton growth rates (as inferred from high fluxes) and lowered nutrients in the surface mixed layer. The evidence from environmental conditions suggests that production at the base of the mixed-layer cannot account for all of the observed cooler $U^{K'}_{37}$ temperature biases. Nutrient levels in summer drop below the concentrations known to cause nutrient-stress responses in the unsaturation levels in culture experiments of alkenone producers (Prahl et al., 2003). These cooler temperatures occur when alkenone fluxes are high. Flux-weighted averages suggest that as much as 80% of alkenone flux in 1996–1997 occurred with $U^{K'}_{37}$ temperature reconstructions cooler than ambient surface temperatures. Annual average SST reconstructions for subtropical waters were 1.5 °C cooler than COADS SST, indicating that "non-calibration" production of alkenones can significantly affect SST reconstructions in these waters.

In subantarctic waters, $U^{K'}_{37}$ temperature biases were to warmer values, and these non-calibration events occurred at times of low flux or at times when the alkenone-producers faced competition from other phytoplankton. Bias to warmer values in $U^{K'}_{37}$ occurs when alkenone synthesis occurs under low light conditions in winter and late summer. Because this non-calibration production was associated with low export fluxes of alkenones, flux-weighted annual average SST reconstructions were only 0.5 °C less than COADS values. Non-calibration production may, therefore, be unimportant in SST paleoreconstructions for these subantarctic waters.

Temporal patterns of phytoplankton sterol fluxes indicated that in both water masses a large spring bloom was followed by a smaller late summer–autumn bloom. Although the spring bloom was observed as 10 fold increases in bulk fluxes (Nodder and Northcote, 2001), in both water masses, the summer/autumn blooms were indistinguishable in the bulk parameters and largely observed in the lipid fluxes at levels comparable to the spring bloom. In subtropical waters, phytoplankton biomarker sterol distributions indicate that diatoms and alkenone-producing haptophytes bloomed synchronously at both times, while dinoflagellates bloomed out of phase with other phytoplankton. In subantarctic waters, the biomarkers indicate a clear species succession sequence among the phytoplankton in both the spring and autumn blooms. Notably, in contrast to subtropical waters, subantarctic alkenone fluxes as a proportion of organic flux were out of phase with diatom export production becoming a higher proportion in the summer and fall. This suggests alkenone producers are outcompeted by diatoms in subantarctic waters in the spring bloom. Additionally, dinoflagellate export production was synchronous with diatom marker fluxes in the spring, but these microalgae were negligible contributors during the autumn bloom.

Our study provides support for the view that physiological response to nutrient and light levels can cause the temperature signal in alkenone-derived proxies in oceanic waters to deviate from known calibrations.

Acknowledgments

This work was begun when ELS was at the Cooperative Research Centre for Antarctic and Southern Ocean Studies, Hobart, Tasmania. This sediment trapping program was achieved via the funding provided to the *Ocean Ecosystems Programme* by the New Zealand Foundation for Research Science and Technology and by an equipment loan arrangement between NIWA and CSIRO, facilitated by Will Howard and Tom Trull. Thanks go to the crew and officers of NIWA's *Tangaroa* and *Kaharoa* and the mooring expertise of Malcolm Greig and Bill Main (both NIWA) and to Matt Pinkerton (NIWA) for providing OCTS ocean color data, courtesy of the Japanese Space Agency. We also thank Stuart Wakeham and an anonymous reviewer for comments that improved the manuscript.

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