

Ecological influences on $\delta^{13}\text{C}$ of particulate matter in seasonally ice-covered Ryder Bay, Antarctica

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Summary Carbon isotopes may be a useful paleoceanographic tool for reconstructing past $p\text{CO}_2$ of surface water, but isotopic composition of particulate organic carbon has been shown in both field and laboratory studies to be affected by $p\text{CO}_2$, growth rate, cell size, cell geometry, light availability, carbon metabolism and species composition. To date, however, field studies have not constrained the dominant factors controlling surface water $\delta^{13}\text{C}_{\text{POC}}$. We present high-resolution time series data from a study in Ryder Bay, Antarctica, which compares seasonal fluctuations in mixed-layer $\delta^{13}\text{C}_{\text{POC}}$ with detailed ecological and morphological analysis of phytoplankton communities, community productivity, source carbon $\delta^{13}\text{C}$, nutrient dynamics, and hydrographic parameters. Preliminary results indicate that physical processes such as ocean-atmosphere gas exchange and upwelling do not significantly affect $\delta^{13}\text{C}_{\text{POC}}$ signatures. In contrast, speciation shifts of diatom assemblages show strong correlation with changes in $\delta^{13}\text{C}_{\text{POC}}$ signals, supporting recent suggestions that taxonomic data are necessary for confident interpretation of sedimentary $\delta^{13}\text{C}$ records.

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Introduction

As a result of its size (~20% of ocean surface) and low-temperature surface waters, the Southern Ocean plays a disproportionately large role in regulating atmospheric carbon dioxide (CO_2) levels, and thus global climate. The main point of gas exchange between ocean and atmosphere (Sarmiento and Toggweiler, 1984), the deep mixed layer and bottom water formation around the Antarctic continent, allows relatively rapid exchange of carbon (Altabet and Francois, 2001). For this reason it has been postulated that on glacial-interglacial time scales the Southern Ocean is primarily responsible for the observed 80-100 ppm variation in atmospheric CO_2 (e.g.: Sarmiento and Toggweiler, 1984). These variations may be driven by physical processes (sea-ice cover, stratification), biological processes (increased photosynthetic productivity), or both (for a review see Sigman and Boyle, 2000).

Constraining the role of the Southern Ocean as a glacial source or sink of CO_2 , and elucidating the influence of physical versus biological marine processes, requires knowledge of ancient CO_2 conditions in surface waters. The $^{13}\text{C}/^{12}\text{C}$ ratio ($\delta^{13}\text{C}$) of dissolved CO_2 reflects its concentration, and this signal is transmitted to phytoplankton as they assimilate carbon (Rau et al., 1989, 1992). The strong correlation between the $\delta^{13}\text{C}$ of particulate organic carbon ($\delta^{13}\text{C}_{\text{POC}}$) and the partial pressure of CO_2 ($p\text{CO}_2$) in the modern Southern Ocean led Rau (1994) to suggest that stable carbon isotopes in marine organic sediments can be used to reconstruct $p\text{CO}_2$ in the surface waters where the material was formed.

Carbon isotopic signature, however, is not a direct function of dissolved carbon concentrations. Growth rate (e.g.: Francois et al., 1993), species variability (Falkowski 1991), carbon metabolism (e.g.: Descolas-Gros and Fontugne, 1990), light availability (Descolas-Gros and Fontugne, 1990; Burkhardt et al., 1999), cell size (Burkhardt et al., 1999), and cell geometry (Popp et al., 1998), all influence isotopic fractionation (ϵ) during the formation of organic matter. Whereas uptake processes are proportional to the cell surface area available as well as permeability, fixation is more closely tied to cellular carbon content, which is often approximated by cell volume (Popp et al., 1998). Popp et al. (1998) showed that cell geometry can affect fractionation by altering surface area to volume ratios, increasing variability of ϵ within size fractions. A recent study of sedimentary organic $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{org}}$) and diatom fossil assemblages by Crosta et al. (2005) indicates that the effects of cell size and shape on $\delta^{13}\text{C}_{\text{POC}}$ are propagated to the sediment record, and can account for a considerable portion of $\delta^{13}\text{C}_{\text{org}}$ variability.

Additionally, taxonomic groups respond differently to fluctuations in $p\text{CO}_2$, due to differences in morphology and physiology (Burkhardt et al., 1999). While most Southern Ocean waters are dominated by diatoms, under certain conditions prymnesiophytes and dinoflagellates may comprise a considerable fraction of algal biomass. However, such taxa are poorly represented in the sedimentary record, as soft tissues are more easily available for water-column remineralization and sedimentary diagenesis, both of which decouple sedimentary records from surface $\delta^{13}\text{C}_{\text{POC}}$ values, complicating the interpretation of $\delta^{13}\text{C}_{\text{org}}$ and reconstructions of $p\text{CO}_2$ (Lourey et al., 2004).

In contrast to surface waters, sea-ice brine is isolated from both surface water and the atmosphere, and is therefore subject only to sporadic nutrient replenishment (Gleitz et al., 1995). Nutrient use as a percentage of the available nutrient pool will be higher, affecting the $\delta^{13}\text{C}$ signal of organic matter. Under high nutrient use conditions, particulate matter is expected to be enriched in ^{13}C relative to phytoplankton from a C-replete environment. Diatoms associated with sea-ice are often small pennate species (Gleitz and Tomas, 1993), and their small size coupled with low nutrient input helps to explain the elevated $\delta^{13}\text{C}_{\text{POC}}$ of sea-ice. In support of this, numerous studies (*e.g.*: Fischer 1991; Gibson et al., 1999; Kennedy et al., 2002) have found that sea-ice algae generally exhibit higher $\delta^{13}\text{C}$ than open-water algae. While several authors have realized the potential of elevated sea-ice $\delta^{13}\text{C}_{\text{POC}}$ to have some bearing on sedimentary records (*i.e.*, Gibson et al., 1999; Lourey et al., 2004; Crosta et al., 2005), the propagation of this isotopic signal from sea-ice to sediments remains poorly understood. Given the much greater extent of sea-ice during glacial periods (Gersonde et al., 2005), constraining this influence would improve our interpretation of sedimentary records.

Project objectives

Despite the many influences on ϵ , Rau et al., (1989, 1992), Francois et al., (1993) and Lourey et al. (2004) have all found a strong correlation between $p\text{CO}_2$ and $\delta^{13}\text{C}_{\text{POC}}$. Identifying what conditions allow small-scale variations in physical conditions or species assemblages to control bulk $\delta^{13}\text{C}_{\text{POC}}$ signals is crucial to confident interpretations of sedimentary proxy records. The aim of this study is to elucidate the principal factors controlling surface-water $\delta^{13}\text{C}_{\text{POC}}$ signatures in a seasonally sea-ice covered environment. We present one of the first high-resolution time series of geochemical parameters coupled with taxonomic phytoplankton data in coastal Antarctic waters. We compare levels of productivity in sea-ice and surface waters with the dissolved CO_2 system, dissolved inorganic carbon isotopes, $\delta^{13}\text{C}_{\text{POC}}$, phytoplankton taxonomy and species composition.

Methods

The Rothera Oceanographic Time Series (RaTS) site was chosen for this study as it provides a long-term, high-resolution data set of hydrographic parameters, and water circulation in this area has been well characterised. The study site ($67^\circ34.02'\text{S}$, $68^\circ14.02'\text{W}$; Figure 1) is located in Ryder Bay, a coastal embayment of Adelaide Island, on the Western Antarctic Peninsula, and is subject to seasonal sea-ice coverage. Water depth is 520 m, and the main surface-water source is from adjacent Marguerite Bay, situated between Adelaide Island and the peninsula.

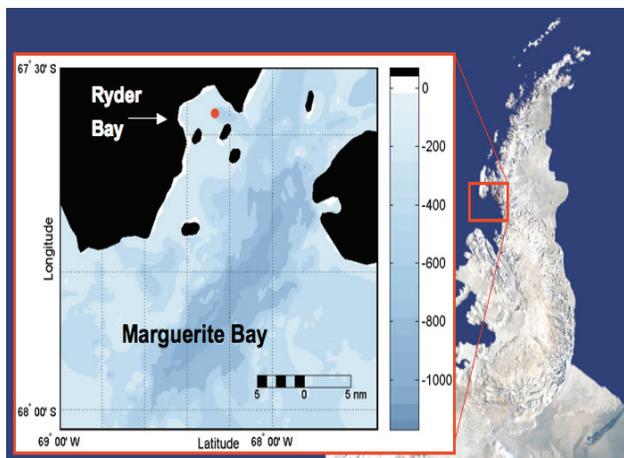


Figure 1. Location of RaTS study site (red marker) in Ryder Bay, and the bathymetry of Ryder Bay and nearby Marguerite Bay on the Western Antarctic Peninsula.

Surface-water samples were collected during the 2004–2007 summer field seasons as weather permitted. Samples for bulk suspended particulates, particulate organic carbon, and $\delta^{13}\text{C}_{\text{POC}}$ were obtained by filtering seawater onto pre-combusted glass fibre filters and drying overnight at 50°C before being frozen. Samples for organic and inorganic nutrients were acidified with HCl and stored frozen until analysis. Isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) and alkalinity (for $p\text{CO}_2$ determination) samples were collected with minimal exposure to atmosphere, and in the case of $\delta^{13}\text{C}_{\text{DIC}}$ treated with CuSO_4 to prevent microbial activity. Samples for taxonomic analysis were filtered onto 37 mm polycarbonate membrane filters (0.45 μm pore size), dried at 50°C and stored in Petri slides. Subsections of each filter were gold-coated for secondary electron imaging. Temperature, salinity, ammonia and chlorophyll *a* data were obtained from the RaTS database (British Antarctic Survey, Cambridge). Sea-ice samples were collected for the same parameters as surface water, by drilling into the ice and collecting the brine.

Preliminary results

Chlorophyll *a*, which is used as a proxy for photosynthetic biomass, shows typically low productivity in the water under the ice, which increases just before the break up of the sea-ice (Figure 2). The spring blooms are periods of elevated production, often comprising two distinct peaks in chlorophyll concentration. The final sampling period (December 2006 to February 2007) was able to capture the transition from ice-covered conditions to open water, although it does not capture the decline of photosynthetic biomass. Seasonal cycles of suspended particulate matter closely followed those of chlorophyll (data not shown).

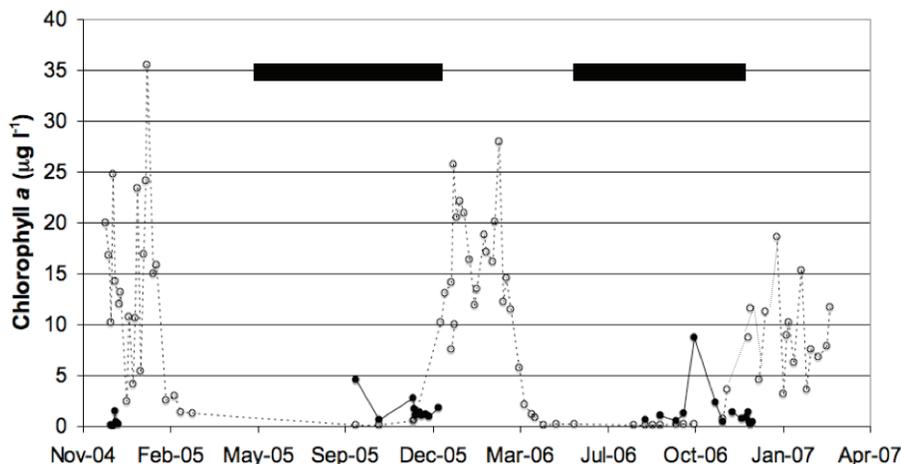


Figure 2. Sea-ice (closed symbols) and surface water (open symbols) chlorophyll *a* at the RaTS study site. Black bars indicate presence of sea-ice.

Isotopic work done in previous seasons indicates a seasonal cycle in $\delta^{13}\text{C}_{\text{POC}}$ in which gradual enrichment is seen over the growing season, with a sharp depletion occurring towards the end of the austral summer (Figure 3). Interestingly, the isotopic composition of source carbon ($\delta^{13}\text{C}_{\text{DIC}}$) exhibits only small variation (1.07 ‰) compared to the >10 ‰ shift in $\delta^{13}\text{C}_{\text{POC}}$. Given the low temperatures, we assume that passive diffusion of DIC across the cell membrane is the primary method of carbon uptake (Rosenthal et al., 2000; Crosta et al., 2005). Thus, if changes in the inorganic carbon pool via processes of upwelling or ocean-atmosphere gas exchange were the principal controls on $\delta^{13}\text{C}_{\text{POC}}$, a significant shift in $\delta^{13}\text{C}_{\text{DIC}}$ would have to occur. The much greater change in $\delta^{13}\text{C}_{\text{POC}}$ indicates that the DIC pool is not the dominant factor influencing this signal.

The depletion of $\delta^{13}\text{C}_{\text{POC}}$ is not accompanied by a similar trend in nitrogen isotopes (data not shown), indicating that the factors controlling carbon and nitrogen fractionation are, at least under certain conditions, decoupled. In addition, the lighter isotopic shift cannot be explained by changes in relative importance of terrestrial-source material, as C:N ratios are invariant throughout the season, and are in close agreement with the marine Redfield ratio of 6:1 (data not shown).

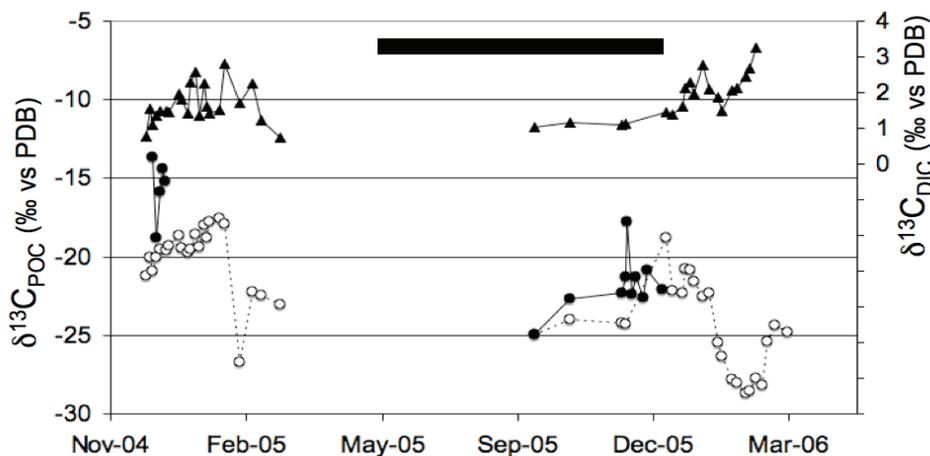


Figure 3. Sea-ice $\delta^{13}\text{C}_{\text{POC}}$ (closed circles) and surface water $\delta^{13}\text{C}_{\text{POC}}$ (open circles) at the RaTS site during the first two field seasons, with isotopic composition of source carbon ($\delta^{13}\text{C}_{\text{DIC}}$; triangles). Black bar indicates presence of sea-ice.

Qualitative analysis of filter samples by scanning electron microscopy indicates that early bloom phytoplankton communities were diverse, with *Chaetoceros* species (*C. socialis*, *C. curvisetus*) and small *Fragilariopsis* species (*F. curta*, *F. cylindrus*) being numerically dominant. Samples collected during the mid-late stage of the bloom, corresponding with $\delta^{13}\text{C}_{\text{POC}}$ depletion, were dominated by *Dactyliosolen* cf. *antarctica* in 2005 and *Proboscia inermis* in 2006. Phytoplankton communities from late bloom periods exhibiting moderate $\delta^{13}\text{C}_{\text{POC}}$ enrichment resembled those

of early bloom conditions, with smaller cells such as *Chaetoceros socialis* and small *Fragilariopsis* species again being most abundant. The changes in diatoms species composition from diverse, small species to nearly monospecific large cells are very tightly coupled to the shifts in $\delta^{13}\text{C}_{\text{POC}}$, and are consistent across the first two seasons. This suggests that factors such as cell size or cell geometry of diatom assemblages may be the primary control on particulate $\delta^{13}\text{C}$ in Ryder Bay surface waters, as both of these variables are known to affect $\delta^{13}\text{C}_{\text{POC}}$. Changes in ϵ associated with growth rate are also a possible cause of the observed $\delta^{13}\text{C}_{\text{POC}}$ fluctuations.

A previous taxonomic investigation by Garibotti et al. (2003) identifies Marguerite Bay as an area of peak chlorophyll concentrations and cell abundances. This mid-late growing season analysis found small unidentified phytoflagellates to be most abundant, although diatoms accounted for ~85% of total biomass (Garibotti et al., 2003). Diatom assemblages at Davis Station have shown a gradual shift from centric to pennate species during austral summer (Perrin et al., 1987). Studies from other coastal Southern Ocean sites have identified the prymnesiophyte *Phaeocystis antarctica* to contribute significantly to surface water biomass at certain points during the season (e.g.: DiTullio et al., 2000).

Unfortunately, samples were not initially collected for taxonomic analysis. Therefore, there are uncertainties associated with calculating absolute abundances of diatom species, and complications arising from inadequate preservation of algal classes lacking rigid cell walls, such as prymnesiophytes. While our relative diatom abundances are robust, we cannot speculate on the influence of class abundances on $\delta^{13}\text{C}_{\text{POC}}$.

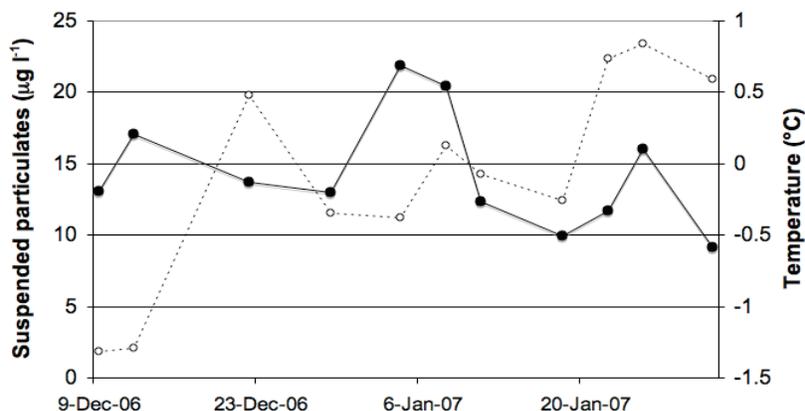


Figure 4. Suspended particulate matter (closed symbols) and temperature (open symbols) at the RaTS study site during the final field season.

To resolve these uncertainties, sampling methods were revised for the final field season, with duplicate water samples preserved with glutaraldehyde and Lugol's iodine solution and kept at 4°C in the dark until analysis. Samples from the most recent field season will allow a detailed evaluation of the role of phytoplankton class dynamics on carbon isotope signals, as well as quantify the shifts in diatom species composition and any associated changes in carbon fractionation.

During the 2006-2007 austral summer, temperature gradually increased with a concurrent decrease in salinity, consistent with the spring ice melt. This gradual change was punctuated by mixing events, causing cold, salty water to be integrated into surface waters through either wind-induced mixing or upwelling. These mixing events are followed by increases in chlorophyll *a* and suspended particulate matter (Figure 4), consistent with the input of nutrients from deeper, nutrient-replete waters.

A further factor, not addressed in this study to date, is how the stable isotopic composition of sedimentary diatom-bound organic matter compares to that of bulk organic matter in sea ice and surface waters. As diatom-bound organic matter is often protected from the effects of remineralization (Rosenthal et al., 2000; Schneider-Mor et al., 2005), capturing this data will confirm whether the isotopic difference in sea ice organic matter and surface-water organic matter is due to post-production processes such as bacterial remineralization or changes in ϵ of diatoms in a sea ice matrix. Work is currently underway to investigate the effects of diatom assemblage, and subsequently $\delta^{13}\text{C}_{\text{org}}$, on the flux of material to the sea floor, through analysis of time series sediment traps and box cores.

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