Major factors controlling Holocene $\delta^{13}C_{org}$ changes in a seasonal sea-ice environment, Adélie Land, East Antarctica

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[1]   In an effort to investigate the controlling factors behind Holocene $\delta^{13}C_{org}$ changes in East Antarctica we report high-resolution down-core records of bulk organic matter carbon isotopic ratios ($\delta^{13}C_{org}$), diatom census counts, total organic carbon, and biogenic silica content taken from one core recovered in the Adélie Trough. A good correspondence between the $\delta^{13}C_{org}$ record and records of small/large and pennate/centric ratios in many of the core segments indicates that diatom species composition affected Holocene $\delta^{13}C_{org}$ variations, possibly via diatom shape and size effects. Variations in the surface water CO_2 concentration and in the isotopic composition of the source during the Holocene cannot be ruled out although they cannot explain rapid and large-amplitude $\delta^{13}C_{org}$ changes. Within the limit of our investigation, our results argue against active carbon acquisition through a carbon concentration mechanism as evidenced in low-latitude upwelling systems. The bulk organic matter thus represents a mixing of diatom taxa having different fractionation affinity to aqueous CO_2. Our results confirm previous evidence which demonstrates that $\delta^{13}C_{org}$ down-core records should be used with great caution to reconstruct past CO_2 content in surface waters.

1.   Introduction

[2]   During the last 2 decades, there has been a considerable debate on the significance of the carbon isotopic ratio of bulk organic matter ($\delta^{13}C_{org}$) and on its usefulness as a proxy of past CO_2 content in surface waters. Pioneering investigations on large oceanic scales have shown that the $\delta^{13}C_{org}$ is anticorrelated with the concentration of molecular dissolved CO_2 ($CO_{2(aq)}$) in surface waters [*Rau et al.*, 1989, 1991]. It was deduced that passive diffusion into phytoplankton cells was the primary carbon acquisition pathway [*Laws et al.*, 1995], and therefore $\delta^{13}C_{org}$ down-core records were tentatively used to reconstruct past CO_2 concentrations in surface waters [*Jasper and Hayes*, 1990; *Bentaleb and Fontugne*, 1998]. However, this relationship has not been consistently observed regionally within a given ocean system when other factors such as growth rate and community structure may become predominant [*Popp et al.*, 1999]. Some investigations of $\delta^{13}C_{org}$ conducted in the Southern Ocean have tried to unravel which of the signals observed were attributable to changes in surface water properties from those of paleoproductivity [*Shemesh et al.*, 1993; *Singer and Shemesh*, 1995; *Rosenthal et al.*, 2000; *Crosta and Shemesh*, 2002],

but even this approach is made uncertain by recent findings on phytoplankton physiology. Today, the debate on $\delta^{13}C_{org}$ significance is centered on the relative impact of cell size/shape changes [*Pancost et al.*, 1997; *Popp et al.*, 1998; *Burkhardt et al.*, 1999; *Trull and Armand*, 2001] and nondiffusive carbon uptake through carbon concentration mechanisms [*Rau*, 2001; *Tortell and Morel*, 2002; *Cassar et al.*, 2004; *Woodworth et al.*, 2004]. Both processes, by strongly affecting the carbon isotopic fractionation (ε_p), loosen the relationship between $\delta^{13}C_{org}$ and $CO_{2(aq)}$, and can account for the discrepancy between marine $\delta^{13}C_{org}$-based pCO_2 reconstructed from low-latitude records and Vostok CO_2 [*Kienast et al.*, 2001]. Most of the investigations highlighting the role of carbon concentration mechanisms in diatoms were conducted in low-latitude upwelling systems or open ocean systems and it is not yet clear whether diatom communities in Antarctic coastal regions are also capable of active transport, and if so if this active uptake is punctual or seasonal.

[3]   As many factors impact on the carbon ε_p, the sedimentary $\delta^{13}C_{org}$ signal is still poorly understood at very high southern latitudes. Additionally, exhaustive investigations of past $\delta^{13}C_{org}$ relevance is noticeably lacking. Here we focus on an exceptionally high-resolution Holocene sediment core of diatom ooze from the Antarctic continental shelf off Adélie Land, East Antarctica. We compare the down-core record of $\delta^{13}C_{org}$ to diatom census counts, organic carbon and biogenic silica content to investigate if any of these factors have controlled or affected the sedi-

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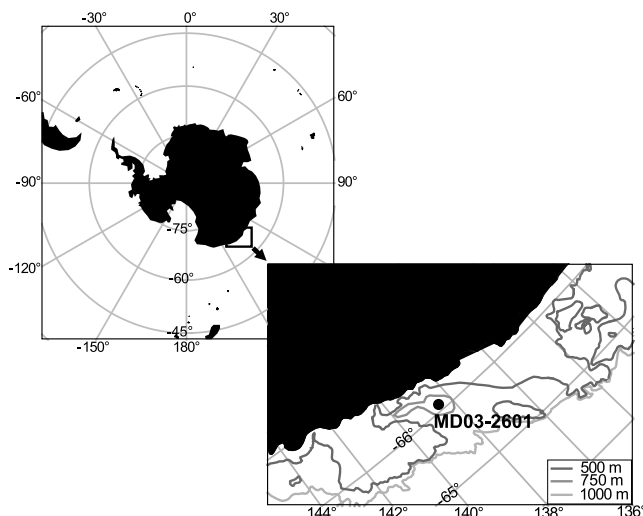
Figure 1. Bathymetric map of the continental margin off Adélie Land (GEBCO source), and location of core MD03-2601.

mentary $\delta^{13}C_{org}$ signal in this region during the last 5000 years.

2. Material and Methods

2.1. Material

[4] Piston core MD03-2601 was retrieved during MD130-Images X cruise (Coring Adélie Diatom Oozes (CADO)) in February 2003 on board R.V. *Marion Dufresne II* with the logistic support of the French IPEV (Institut Paul Emile Victor). Core MD03-2601 was retrieved at $66°03.07'S$, $138°33.43'E$ in 746 m water depth in one of the small depressions composing the D'Urville Trough (Figure 1). The Trough incises the shelf out to the shelf break and is bounded to the east by the Adélie Bank and to the west by the Dibble Bank. The trough has an average depth of 600–700 m and consists of a series of small depressions reaching a maximum depth of 900–1000 m [*De Santis et al.*, 2003]. These depressions act as funnels, which focus the phytoplankton cells (mainly diatoms [*Wright and van den Enden*, 2000]) produced in the area, thereby increasing their preservation efficiency. Core MD03-2601 is composed of diatom ooze alternating between structureless greenish ooze and green-to-dark green laminations of millimeter to centimeter thickness.

2.2. Stratigraphy

[5] Three radiocarbon dates have been performed on the green material humic fraction of bulk organic matter at the Leibniz Laboratory, Kiel, Germany. The residual material was extracted with 1% HCl, 1% NaOH at 60°C and again 1% HCl. The alkali extract (humic acid fraction) was precipitated with HCl, washed, and dried. The combustion to CO_2 of all fractions was performed in a closed quartz tube together with CuO and silver wool at 900°C. The sample CO_2 was reduced with H_2 over ~2 mg of Fe powder as catalyst, and the resulting carbon/iron mixture was pressed into a pellet in the target holder. The ^{14}C concen-

tration of the samples was measured by comparing the simultaneously collected ^{14}C, ^{13}C, and ^{12}C beams of each sample with those of Oxalic Acid standard CO_2 and coal background material. Conventional ^{14}C ages were calculated according to *Stuiver and Polach* [1977] with a $\delta^{13}C$ correction for isotopic fractionation based on the $^{13}C/^{12}C$ ratio measured by our AMS-system simultaneously with the $^{14}C/^{12}C$ ratio.

[6] Raw ^{14}C dates indicate that the core covers the parts of the Mid-Holocene and Late Holocene periods. Raw ^{14}C dates were corrected by a 1300-year reservoir age effect [*Ingólfsson et al.*, 1998] which provides average sedimentation rates of 0.88 cm yr^{-1} between 2050 and 998 cm and 0.35 cm yr^{-1} between 998 and 0 cm (Table 1), in agreement with early investigations of East Antarctica sediments [*Domack*, 1988].

2.3. Isotopic and Elemental Analysis

[7] Isotopic measurements were done every 4 cm to 8 cm. The raw sediment was decarbonated with a 1 N HCl solution for 15 min at 65°C. The carbonate free fraction was then rinsed 3 times with milli-Q water and oven dried. Carbon isotopic measurements were performed on a Carlo Erba 2500 elemental analyzer in line with a VG Isoprime at UMR EPOC (France). The mean standard deviation is 0.1‰ for the $\delta^{13}C_{org}$. All results are reported in δ notation versus PDB, and were checked for internal consistency using several calibrated laboratory standards such as Acetanilid, Glycine and Casein. Organic carbon content (C_{org}) was measured simultaneously with the isotopic ratios by integrating the voltage of the main ion beam. The mean standard deviation of the carbon content is ±0.03%.

2.4. Diatom Analysis

[8] Diatoms were taxonomically identified every 4 to 8 cm following the sample intervals of the geochemical analysis. Diatom analysis, sediment treatment and slide preparation followed the technique described by *Rathburn et al.* [1997]. Diatom counts followed *Schrader and Gersonde* [1978] and *Laws* [1983]. Around 350 diatom valves were counted in each sample at a magnification of 1250. Diatoms were identified to species or species group level, and the relative abundance of each was determined as the fraction of diatom species against total diatom abundance in the sample. More details about slide preparation, diatom identification and statistical treatment are given by *Crosta et al.* [2004].

2.5. Biogenic Silica Content

[9] Biogenic silica (BioSi) measurements follow a protocol slightly modified from *Mortlock and Froelich* [1989] in

Table 1. Accelerator Mass Spectrometry ^{14}C ages From Core MD03-2601[a]

Depth, cm	^{14}C Ages ±1σ, years B.P.	Corrected ^{14}C Ages, years B.P.	Sedimentation Rate, cm per year
2	2350 ± 40	1050	
998	5175 ± 40	3875	0.35
1998	6310 ± 60	5010	0.88

[a]Ages were corrected by a constant age reservoir of 1300 years (*Ingólfsson et al.*, 1998).

which biogenic silica was dissolved in a 0.5 M NaOH solution. Absorbance of the samples was measured each hour for 5 hours to build a dissolution curve [*Müller and Schneider*, 1993] and then calibrated using five standards of increasing silica concentration and a blank. Biogenic silica is determined with the following equation:

$$\%_{\text{mass}} SiO_2 = [SiO_2] \times ((0.5/A) \times V \times M \times 0.0001)/m,$$

where $[SiO_2]$ = ((absorbance – y intercept)/slope) of the calibration curve; A is the volume of the aliquot taken from the centrifuge tubes (0.25 mL); V is the volume of NaOH added in the centrifuge tubes (40 mL); M is molar mass of silica (60.1 g.mol^{-1}); 0.0001 = 1.10^{-6} g/µg × 100%; and m is sample mass in mg.

[10] Biogenic silica was analyzed in duplicates every 32 cm with a ∼1% standard error on the whole protocol.

3. Results

[11] We produced high-resolution records of $\delta^{13}C_{\text{org}}$, C_{org} content and diatom census counts, and a low-resolution record of biogenic silica. The records cover the last 5050 radiocarbon reservoir corrected years with a temporal resolution of 15–100 years depending on the proxy. However, we do not focus on paleoclimatic reconstructions that require better chronologic control but on understanding the factors that have controlled the $\delta^{13}C_{\text{org}}$ signal in the Adélie Land region during the Holocene.

[12] The down-core record of $\delta^{13}C_{\text{org}}$ shows absolute variation of 3‰ from −24.8‰ at 1064 cm to −27.8‰ at 52 cm (Figure 2a). The $\delta^{13}C_{\text{org}}$ values are around −25.5‰ between 2050 and 1064 cm (5050–3955 yr B.P.) and are progressively depleted until 600 cm depth (2745 yr B.P.). At depths above 600 cm, $\delta^{13}C_{\text{org}}$ values are around −26.5‰ except at an interval of enriched values between 424 and 268 cm (2245–1805 yr B.P.). Large-amplitude variations of $\delta^{13}C_{\text{org}}$ at a scale of about 1 m and smaller amplitude variations of about a half meter are superimposed on the long-term $\delta^{13}C_{\text{org}}$ trend along the length of the core.

[13] Relative abundances of the main sea-ice diatoms, the *Fragilariopsis curta* group as defined by *Gersonde and Zielinski* [2000], are ∼10% between 2050 and 1120 cm and sharply increase to ∼30% in 60 cm (Figure 2b, black line). The *F. curta* group subsequently presents elevated relative abundances around 30% until the top of the core. Rapid variations at several scales from 2 m to 50 cm are superimposed onto the Holocene trend. Relative abundances of the main open-ocean diatom, *F. kerguelensis*, follow an opposite pattern to the *F. curta* group. *Fragilariopsis kerguelensis* represents ∼15–20% of the diatom assemblage between 2050 and 1120 cm and sharply decreases to 5% in 60 cm (Figure 2b, gray line). Relative abundances of *F. kerguelensis* subsequently remain low around 5–10% till the top of the core. The same rapid variations of *F. kerguelenisis* are observed down core as with the *F. curta* group. The diatom record in core MD03-2601 allows us to clearly divide the Holocene in two periods: a warm period that represents a part of the Mid-Holocene Climatic Optimum (MHCO) between 2050 and 1120 cm and a cool period that represents the Late-Holocene Neoglacial (LHN) between 1080 and 0 cm. The sharp transition between these two periods, centered around 4000 yrs B.P., occurs within 50 years.
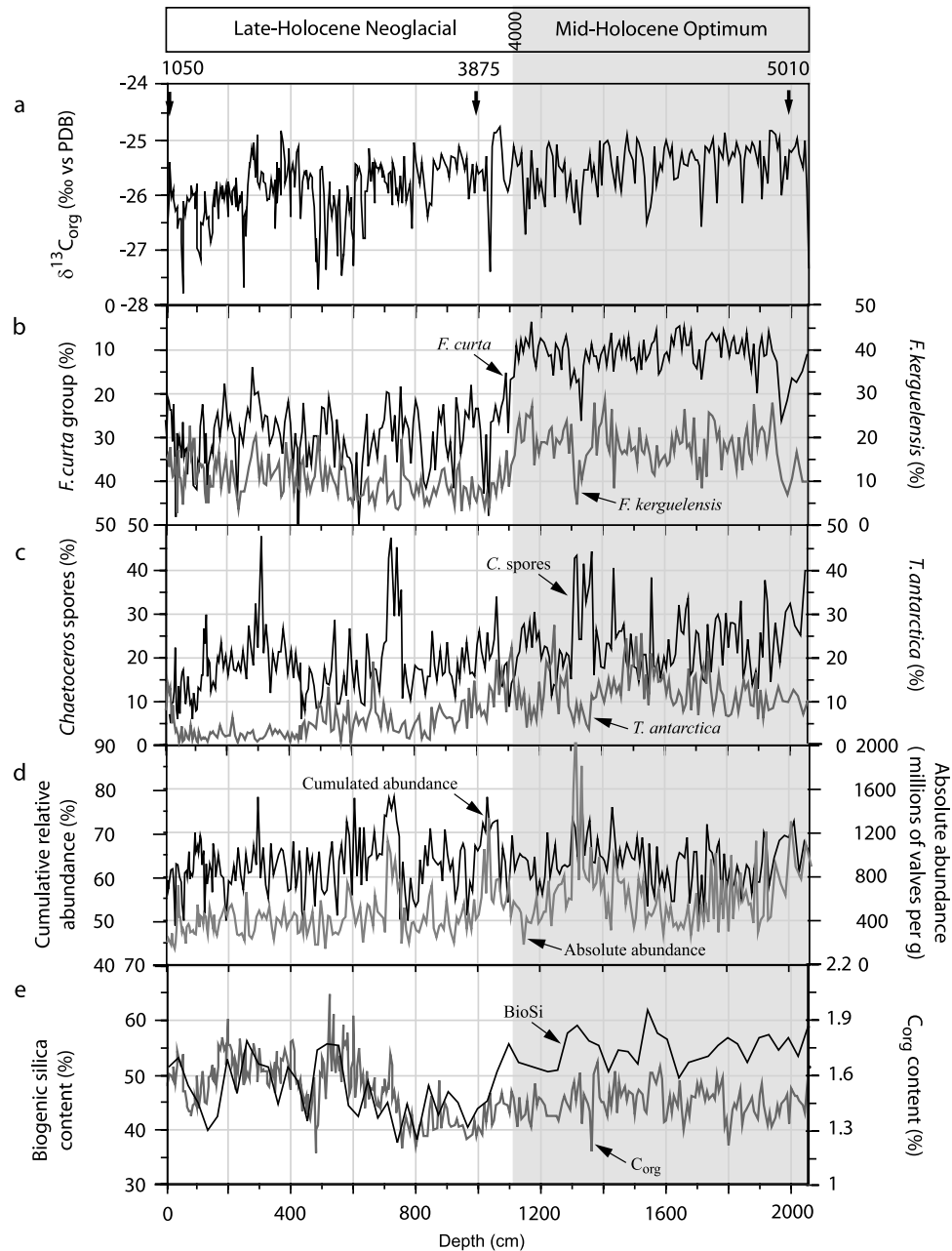
[14] The *Chaetoceros* resting spores group represents a highly variable fraction of the diatom assemblages (Figure 2c, black line) from 5% to 55%. We note that the average relative abundances of this group are higher in the MHCO than during the LHN. Similarly, *Thalassiosira antarctica* relative abundances are elevated during the MHCO in contrast to the LHN period, where occurrences are observed at ∼10–15% and <10%, respectively, for each period (Figure 2c, gray line). Cumulated relative abundances of these four species or species groups represent around 60–70% of the total diatom assemblage with no discernable Holocene trend (Figure 2d, black line). However, these four species/species groups are highly representative of the whole diatom assemblage and give a significant picture of the oceanic environmental changes off Adélie Land.

[15] Absolute diatom abundances are on average 600 millions of valves per gram of dry sediment during the MHCO with the peak abundance of 2000 million of valves at 1320 cm due to a high occurrence of *Chaetoceros* resting spores (Figure 2d, gray line). Absolute diatom abundances decrease during the LHN with an average value of 400 million of valves per gram of dry sediment, with exception to two abundance maxima of ∼1000 millions of valves per gram at 1040 cm and 720 cm core depth.

[16] Biogenic silica content (BioSi) oscillates around 55% between 2050 and 1100 cm and sharply decreases at the MHCO-LHN transition (Figure 2e, black line). Biogenic silica content then amounts for ∼40% between 1000 and 750 cm and subsequently increases again to regain 50–55% in the upper portion of the core. Low BioSi content is discernable at 450 cm and 150 cm. There is no relationship between BioSi and absolute diatom abundances in core MD03-2601. Conversely, there is a good relationship between BioSi and relative abundances of heavily silicified diatoms. The organic carbon content (C_{org}) varies between 1.2% and 2.1% of the dry sediment weight (Figure 2e, gray line). The C_{org} record is strongly correlated to the BioSi record both in the timing and in the amplitude of the changes in each period. However, the C_{org} increase at 750 cm is much more pronounced than the BioSi increase, which obtains higher values during the MHCO. This decoupling may be related to better C_{org} preservation above 750 cm, which are related to suboxic conditions as evidenced by a clear agreement between C_{org} and sulphur content measured on the XRF core-Scanner of Bremen University, Germany (data not shown here).

4. Discussion

[17] We have produced a high-resolution record of $\delta^{13}C_{\text{org}}$ for comparison with other high-resolution records from the same core to investigate whether community structure, productivity or environmental conditions have controlled Holocene $\delta^{13}C_{\text{org}}$ changes off Adélie Land. This sedimentary record perspective cannot take into account more specific biological processes such as cell wall CO_2 perme-

Figure 2. Down-core records in core MD03-2601 versus depth, (a) $\delta^{13}C_{org}$, (b) relative abundances of the *F. curta* group (black line) and *F. kerguelensis* (gray line), (c) relative abundances of *Chaetoceros* resting spores (black line) and *Thalassiosira antarctica* (gray line), (d) cumulated relative abundances of the four diatom species mentioned above (black line) and absolute abundance of diatoms in millions of valves per gram of dry sediment (gray line), and (e) biogenic silica content (black line) and organic carbon content (gray line). Arrows and associated numbers represent radiocarbon dates corrected for the reservoir age as indicated in Table 1.

ability and Rubisco selectivity. However, these processes may be species dependent, and therefore difficult to unravel from diatom size/shape effects. The main inorganic carbon source is here hypothesized to be molecular CO_2. This is not the case for low-latitude upwelling systems where the prevalent inorganic carbon source is HCO_3^- as part of a carbon concentration mechanism [*Rau*, 2001; *Tortell and Morel*, 2002; *Woodworth et al.*, 2004]. However, this active HCO_3^- acquisition is enhanced at low CO_2 levels [*Tortell et al.*, 2000] and results in low ε_p and enriched $\delta^{13}C_{org}$ values
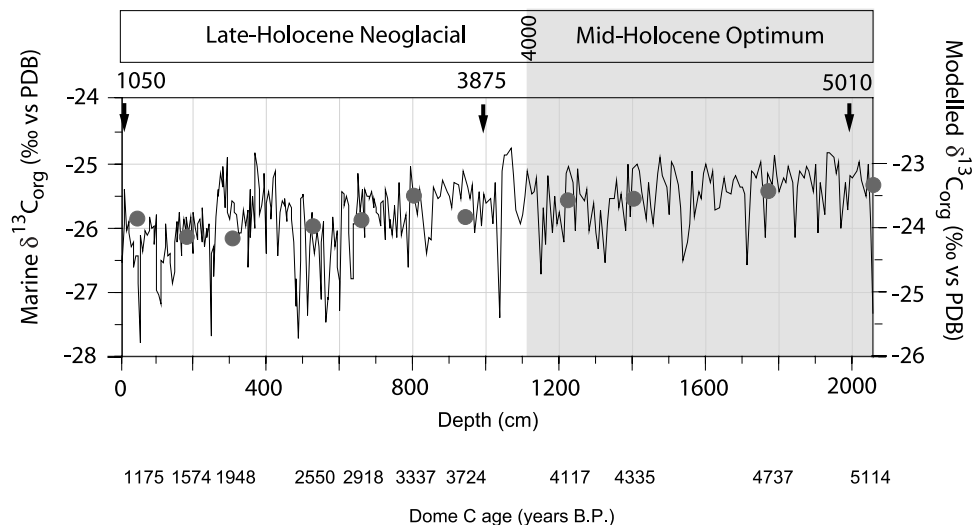
Figure 3. Comparison between the $\delta^{13}C_{org}$ record in core MD03-2601 versus depth (black line) and the modeled $\delta^{13}C$ of particulate organic matter (gray dots) calculated at equilibrium using the Holocene atmospheric CO_2 concentration and temperature changes recorded at EPICA Dome C [*Fluckiger et al.*, 2002; *Masson-Delmotte et al.*, 2004], a temperature-dependent CO_2 solubility constant [*Weiss*, 1974], and the equation calculated from the SR3 transect [*Popp et al.*, 1999] versus age (gray dots). Dome C ages were replaced onto MD03-2601 timescale as extrapolated between the corrected ^{14}C dates. Dome C ages respective to the calculated $\delta^{13}Corg$ are reported at the vertical of each point. Arrows and associated numbers represent radiocarbon dates corrected for the reservoir age as indicated in Table 1.

[*Woodworth et al.*, 2004]. The surface waters of the high southern latitudes are saturated in CO_2 [*Takahashi et al.*, 2002], whereby measured ε_p are elevated [*Rau et al.*, 1989] and measured $\delta^{13}C_{org}$ are depleted [*Cremer et al.*, 2003] compared to low-latitude environments. These findings may indicate that carbon acquisition in our study area is achieved mainly through passive diffusion of molecular CO_2, hence a potential rationale to the observed relationship between $\delta^{13}C_{org}$ and $CO_{2(aq)}$ on the SR3 transect between Tasmania and Adélie Land [*Popp et al.*, 1999].

[18] A first approximation of CO_2 concentration in surface waters off Adélie Land can be calculated using the Holocene atmospheric CO_2 concentrations and Holocene temperature changes recorded at EPICA Dome C [*Fluckiger et al.*, 2002; *Masson-Delmotte et al.*, 2004] and a temperature-dependent CO_2 solubility constant [*Weiss*, 1974]. Surface water CO_2 concentrations are subsequently translated into $\delta^{13}C_{org}$ using the equation calculated from the SR3 transect as presented by *Popp et al.* [1999]. Temperature changes are small during the Holocene leading to little variation of the CO_2 solubility constant. As a result, calculated $\delta^{13}C_{org}$ is driven by atmospheric changes that increase smoothly during the Holocene. The calculated $\delta^{13}C_{org}$, therefore, decreases gradually by 0.8‰ during the last 5000 years from −23.4‰ to −24.2‰ (Figure 3). The down-core record of $\delta^{13}C_{org}$ follows a similar decreasing trend during the last 5000 years but additionally presents rapid variations of 2– 3‰ of amplitude. Such large-amplitude variations, which require a temperature change of about 5°C, cannot be accounted for by the slow atmospheric CO_2 evolution or by small temperature changes as recorded in ice cores.

[19] The isotopic signature of the inorganic carbon can influence the $\delta^{13}C_{org}$. Holocene fluctuations of inorganic

carbon $\delta^{13}C$ can be inferred from carbon isotopic ratio measurements in benthic foraminifera ($\delta^{13}C_{benth}$). However, studies of $\delta^{13}C_{benth}$ are restricted to the Antarctic Peninsula and interpretations might not be directly extrapolated to East Antarctica because the latter region is more remote from the Antarctic Circumpolar Current and the westerly wind system that drive bottom water ventilation in the Antarctic Peninsula region [*Shevenell and Kennett*, 2002]. Additionally, primary productivity and bottom water formation can affect the $\delta^{13}C_{benth}$ signal [*Mackensen et al.*, 1990, 1994]. Keeping this in mind, the $\delta^{13}C_{benth}$ recorded in Antarctic Peninsula sediments shows strong variations of about 0.8‰. Changes in the isotopic signature of the carbon source may therefore account for a third of the $\delta^{13}C_{org}$ variations. However, low $\delta^{13}C_{benth}$ resolution and different reservoir ages established around Antarctica [*Ingólfsson et al.*, 1998] preclude direct comparison of the two records and further interpretation.

[20] Several marginal marine systems such as the Ross Sea present different microalgal dominances in relation to the mixed layer depth. Diatoms dominate in strongly stratified waters whereas the nonsiliceous cryptophyte microorganism, *Phaeocystis antarctica*, dominates in well-mixed waters [*Arrigo et al.*, 1999]. Different phytoplankton groups have different mean ε_p slopes [*Popp et al.*, 1998], carbon to volume content [*Menden-Deuer and Lessard*, 2000] and nutrient requirements [*Sambrotto et al.*, 2003]. Microalgal community changes, therefore, affect the carbon isotopic ratio of suspended and buried organic matter. It is essential then to document down-core changes in the community structure of core MD03-2601 to determine whether community variability has a strong impact on the $\delta^{13}C_{org}$ record. In core MD03-2601, the carbon content (C_{org}) record is strongly correlated to the biogenic silica

content (BioSi) record in the first 1000 cm of the core both in the timing and in the amplitude of the changes (Figure 2e). This indicates that diatoms were the dominant phytoplankton group during the last 3875 years, in agreement with the modern community structure off Adélie Land [*Wright and van den Enden*, 2000]. Deeper than 1000 cm, both records are still in phase and present variations with similar amplitude but the global increase in BioSi is not reflected in the C_{org} signal. Again here, the synchronization in the content changes and their similar amplitudes indicate that diatoms remained the dominant phytoplankton group between 3875 and 5050 years B.P. The jump in the C_{org} to BioSi ratio at 4000 years B.P. may be related either to (1) a shift in diatom dominance (Figure 2b) where the *Fragilariopsis curta* group with elevated Corg to BioSi [*Friedrich and van der Loeff*, 2002] dominated during the LHN and *F. kerguelensis* with low Corg to BioSi [*Friedrich and van der Loeff*, 2002] dominated during the MHCO, or (2) a better preservation of C_{org} during the LHN because of reduced oxidative conditions. The shift in diatom dominance from the open ocean preferring *F. kerguelensis* to that of the sea-ice dominant *F. curta* group is related to changes in environmental conditions from lesser to greater sea-ice cover at the MHCO-LHN transition dated around 5000 calendar years B.P. in other regions of the Southern Ocean [*Porter*, 2000; *Hodell et al.*, 2001]. The correspondence between C_{org} and BioSi records in core MD03-2601 indicates that changes in the community structure from siliceous to non-siliceous organisms were certainly small. Diatom dominance in the sedimentary record undoubtedly explains the relative constancy of the $\delta^{13}C_{org}$ record during the last 5050 years. The observed $\delta^{13}C_{org}$ variations in core MD03-2601 may be linked to biological processes internal to the diatom community, such as productivity, presence/absence of depleted sea-ice species or differences in size fraction.

[21] In core MD03-2601, productivity changes are tracked by the down-core relative abundance records of *Chaetoceros* resting spores (CRS) and *T. antarctica*. *Chaetoceros* vegetative cells thrive in areas of high nutrient content such as Antarctic coastal regions and low-latitude upwelling systems. Resting spores are formed when environmental conditions become unfavorable due to low light levels or nutrient depletion after intense blooms [*Hargraves and French*, 1975; *von Bodungen et al.*, 1985]. Resting spores are therefore taken as an indication of very strong spring productivity events that rapidly deplete surface water nutrients [*Leventer*, 1991] and have been widely used to estimate past changes in productivity [*Leventer et al.*, 1996; *Taylor et al.*, 2001]. The species *T. antarctica* is associated with polynyas or unconsolidated sea-ice conditions [*Leventer et al.*, 1996; *Armand et al.*, 2005] and are indicative of high productivity during the summer and autumn seasons. Through the Holocene, a general decreasing trend of CRS and *T. antarctica* relative abundances occurs toward modern times comparable to the $\delta^{13}C_{org}$ trend. Nevertheless, events of large CRS depositions at 296 cm, 716–732 cm and 1312–1360 cm, or of greatest *T. antarctica* accumulations are not always concomitant to the enriched $\delta^{13}C_{org}$ values (Figure 2c). Additionally, other indicators of paleoproductivity such as BioSi and C_{org}

content records are decoupled from the $\delta^{13}C_{org}$ signal. Such an effect may be due to dilution of the sedimentary record by terrigenous input or variable C_{org} and BioSi preservation. Therefore we argue that carbon demand via biological uptake does not represent the main control on Holocene $\delta^{13}C_{org}$ variations off Adélie Land.

[22] Sea-ice diatoms are known to be depleted in ^{13}C [*Fisher*, 1991]. Our strong match between the *F. curta* group abundance and the $d^{13}C_{org}$ records (R = −0.46, n = 275) indicates that the ratio of sea-ice diatoms to the total diatom assemblage almost certainly influences the $\delta^{13}C_{org}$ of settling particles (Figure 2b, black line). Both pennate-shaped diatoms, the *F. curta* group and *F. kerguelensis*, capture rapid changes of the $\delta^{13}C_{org}$ signal, but similarly both diatom records fail to capture the gradational change observed in the $\delta^{13}C_{org}$ record over the last 5000 years (Figure 2b). Centric diatoms, mainly represented in core MD03-2601 by the CRS group and *T. antarctica*, present a reverse situation. Their relative abundances present rapid variations that are not concurrent to the $\delta^{13}C_{org}$ rapid changes but alternatively, they capture the gradational trend of the $\delta^{13}C_{org}$ signal (Figure 2c). We hypothesized then that diatom size/shape is an important control on the carbon isotopic composition of the organic matter preserved in the Adélie Trough. Indeed, during the SOIREE iron release experiment at 61°S, 140°E, phytoplankton cell size was found to be the dominant control of sinking particles $\delta^{13}C_{org}$ [*Trull and Armand*, 2001] because small diatoms generally have a greater carbon isotopic fractionation than large diatoms as a result of different surface-to-volume ratios and cellular carbon content [*Pancost et al.*, 1997; *Popp et al.*, 1998; *Burkhardt et al.*, 1999].

[23] Two proxies of diatom size/shape changes were then compared to the $\delta^{13}C_{org}$ down-core record to investigate the potential impact of diatom size fraction on the isotopic signal (Figure 4). The threshold between small and large species was fixed at 25–30 μm both for pennate and centric diatoms (Table 2). The record of small-to-large diatoms (S/L) agrees well with the $\delta^{13}C_{org}$ record, especially between 2050 cm and 600 cm depth (Figure 4a). S/L rapid variations present a similar cyclicity to those of the $\delta^{13}C_{org}$ record, while events of abundant small diatoms at 1432 cm, 1312 cm, 1032 cm, 848 cm, 732 cm, 668 cm and 598 cm are generally concomitant to depleted carbon isotopic values. This fit argues for a role of cell geometry on the control of carbon isotopic fractionation in diatoms as previously identified in culture experiments [*Popp et al.*, 1998]. A simple fit the S/L and $\delta^{13}C_{org}$ records however produces a correlation coefficient of only −0.28 (n = 275). The low R value may result from the difficulty of assigning a specific group size to species that are within the limit of the two size categories selected here. A low R value may also indicate that diatom size is not enough to account for the species-specific factors that control the carbon ε_p. Indeed, small pennate diatoms such as the *F. curta* group have different surface-to-volume ratios and cellular carbon content than other small centric diatoms such as *Chaetoceros* resting spores.

[24] The record of pennate-to-centric diatoms (P/C) shows a similar progression in comparison to the $\delta^{13}C_{org}$ record in
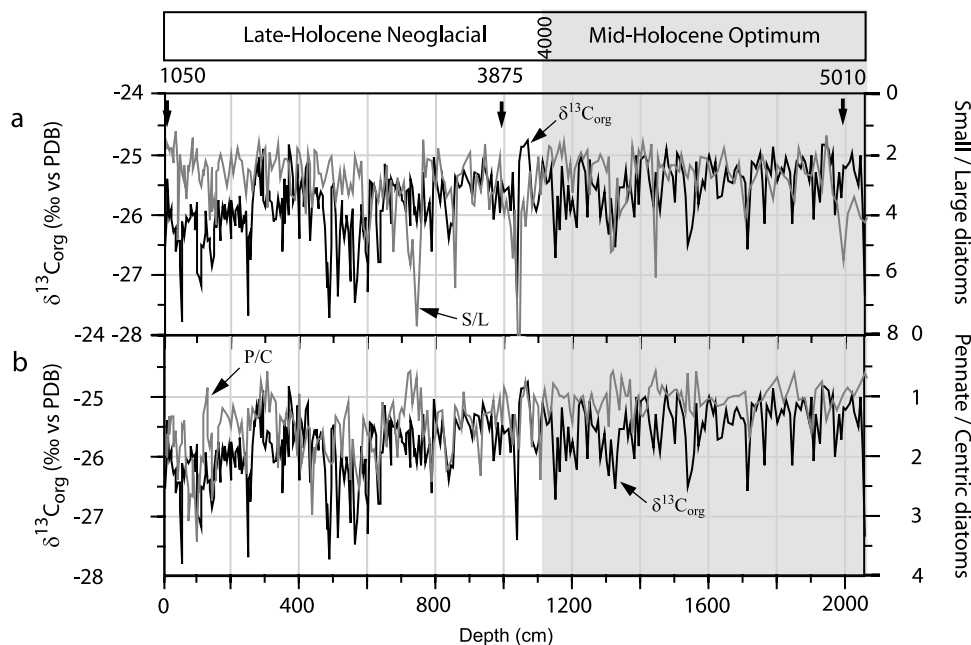
Figure 4. Down-core records in core MD03-2601 versus depth, (a) $\delta^{13}C_{org}$ (black line) and ratio of small-to-large diatoms (gray line) and (b) $\delta^{13}C_{org}$ (black line) and ratio of pennate-to-centric diatoms (gray line). Groups of diatoms are defined in Table 2. Arrows and associated numbers represent radiocarbon dates corrected for the reservoir age as indicated in Table 1.

core MD03-2601, both in the rapid changes and in the Holocene gradational trend (Figure 4b). High P/C ratio values are generally simultaneous with depleted values of $\delta^{13}C_{org}$, while low ratio values are generally in phase with enriched values of $\delta^{13}C_{org}$. Such an observation is in agreement with pennate diatoms having greater ε_p than centric diatoms, hence resulting in lighter $\delta^{13}C_{org}$ values when pennate species dominate the diatom assemblage. The P/C record is the only proxy here that perfectly captures the large amplitude $\delta^{13}C_{org}$ peak around the MHCO-LHN transition. It also captures the strong $\delta^{13}C_{org}$ variability above 600 cm that the S/L ratio failed to reproduce. The good fit between the P/C ratio and the $\delta^{13}C_{org}$ records results in a correlation coefficient of -0.43 (n = 275), which indicates that diatom shape is possibly the most important factor studied here, controlling the carbon isotopic ratio of sinking organic particles in the seasonal sea-ice environment off Adélie Land. This finding may be related to species-specific relationships between ε_p and the dissolved inorganic carbon concentration in surface waters in response to different surface-to-volume ratios and carbon content. It is possible that physiological processes such as cell wall permeability and Rubisco selectivity are size/ shape dependent but this cannot be demonstrated here. The relationship between the P/C ratio and the $\delta^{13}C_{org}$ records is not consistent all core long. Intervals of disagreement may represent periods when factors other than diatom size/shape dominate or codominate the $\delta^{13}C_{org}$ signal. One important process in low-latitude upwelling systems is active carbon transport [*Rau*, 2001; *Tortell and Morel*, 2002]. It is possible that the proportion of active

acquisition to passive diffusion also becomes dominant in Antarctic waters, especially when diatoms need to maintain elevated growth rates. Whether this process is seldom or common, punctual or seasonal is not known. Additional

Table 2. Summary of the Diatom Groups Separated by Shape and Size[a]

Shape	Size	Group
Pennates	small, <25–30 μm	*Fragilariopsis curta* group
		F. rhombica
		F. separanda
Pennates	large, >25–30 μm	*F. kerguelensis*
		F. obliquecostata
		F. ritscheri
		F. sublinearis
Centrics	small, <25–30 μm	*Chaetoceros* vegetative
		C. resting spores
		Thalassiosira antarctica
		T. gracilis
Centrics	large, >25–30 μm	*Actinocyclus actinochilus*
		Corethron cryophilum
		Eucampia antarctica
		Porosira glacialis group
		Proboscia spp.
		Rhizosolenia spp.
		Stellarima microtrias
		T. lentiginosa
		T. tumida

[a]Cumulated relative abundances of the species or species groups defined above represent more than 95% of the total diatom assemblage. Rare diatoms or unidentified specimens were not used in the calculation of the small-to-large and pennate-to-centric diatom ratios.

investigations of modern processes in the water column and at the water-sediment interface in the seasonal sea-ice zone are needed to answer this question.

5. Conclusions

[25] We compare a high-resolution record of $\delta^{13}C_{org}$ to records of diatom census counts, organic carbon and biogenic silica content in one core retrieved in the Adélie Trough, East Antarctica, to investigate which factors have influenced $\delta^{13}C_{org}$ variability during the last 5000 years. Although unique in approach, this kind of investigation cannot take into account physiological processes such as active carbon uptake, cell wall permeability and Rubisco selectivity that are important in low-latitude upwelling systems [*Tortell et al.*, 2000; *Rau*, 2001; *Woodworth et al.*, 2004]. Within the limitation of our study, variations in diatom species composition appear to have played an essential role in the Holocene $\delta^{13}C_{org}$ changes from the coastal sea-ice zone, and this to some degree relates to species-specific size/shape and surface area/volume effects as suggested by laboratory experiments [*Popp et al.*, 1998; *Burkhardt et al.*, 1999] and by previous water column studies from the Antarctic open ocean zone [*Popp et al.*, 1999; *Trull and Armand*, 2001]. However, we reckon that exhaustive investigations coupling the water column, the water-sediment interface and long sedimentary records, are required in the seasonal sea-ice zone to better understand the sedimentary $\delta^{13}C_{org}$ records from the Antarctic continental shelf. Our study anyway indicates that $\delta^{13}C_{org}$ records from the Antarctic continental shelf may be used with caution to reconstruct past CO_2 content in surface waters and in the atmosphere as has been reported previously in the low latitudes [*Kienast et al.*, 2001].

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