

Quantifying habitat-specific diatom production: A critical assessment using morphological and biogeochemical markers in Antarctic marine and lake sediments

Elie Verleyen

Lab. Protistology and Aquatic Ecology, Ghent University, Krijgslaan 281-S8, 9000 Gent, Belgium

Dominic A. Hodgson

British Antarctic Survey, Natural Environment Research Council, High Cross, Madingley Road, Cambridge CB3 0ET, Great Britain

Peter R. Leavitt

Limnology Laboratory, Department of Biology, University of Regina, Regina, Saskatchewan S4S 0A2, Canada

Koen Sabbe and Wim Vyverman

Lab. Protistology and Aquatic Ecology, Ghent University, Krijgslaan 281-S8, 9000 Gent, Belgium

Abstract

Reconstructions of historical primary production, and of the algal groups and habitats that contribute to it, are fundamental in studies of climate and environmental change in both marine and freshwater environments. The aims of this study were to critically evaluate morphological and biogeochemical markers of diatom production by direct comparison of diatom marker pigments with absolute diatom biovolume and to partition diatom production between the main habitats (plankton, sea ice, and benthos). Sediments in two cores from the Larsemann Hills, Antarctica, spanning the last 10,000 yr, were analyzed for siliceous microfossils by microscopy and for fossil pigments by high-performance liquid chromatography. Diatom pigments (diadinoxanthin, diatoxanthin, fucoxanthin) were highly correlated ($r^2 = 0.557$ and 0.358 , $p < 0.0001$) with diatom biovolume in the marine intervals of both cores, but only weakly correlated in the lacustrine sections ($r^2 = 0.102$, $p = 0.111$; $r^2 = 0.223$, $p = 0.001$, after correction for temporal autocorrelation), possibly because of frustule dissolution and selective degradation of diadinoxanthin and diatoxanthin. In contrast, fucoxanthin was better preserved. By combining both microfossil and pigment proxies, we obtained a first estimate of diatom production in specific habitats (benthic and planktonic). Benthic diatom production was greatest in the lacustrine core sections, when benthic microbial mats dominated the flora, whereas diatoms were associated mainly with the water column and sea ice during the marine intervals. The combination of both proxies in marine and freshwater environments permits more accurate interpretation of pigment and diatom data in paleo- and neocological research and the partitioning of diatom production between habitats.

The reconstruction of primary production and identification of the taxonomic groups that contribute to it are fundamental components in many paleolimnological and paleoceanographic studies. However, because only a small number of autotrophic organisms deposit recognizable morphologi-

cal fossils (e.g., diatoms, chrysophytes, and coccolithophore bearing haptophytes), biogeochemical markers such as fossil pigments have been used widely as proxies of past and present production and algal community composition (e.g., Verschuren et al. 1999; Bianchi et al. 2002a). Fossil pigments have shown their potential in a diversity of applications as indicators of algal and bacterial composition, food web interactions, lake acidification, mass flux within lakes, past ultraviolet (UV) radiation, and a wide range of anthropogenic activities (Leavitt and Hodgson 2001). Although pigments are often reliable proxies of algal production, differential preservation of compounds in sediments can prevent quantitative reconstruction of algal community composition, as is commonly done in modern investigations (e.g., CHEMTAX, Mackey et al. 1996).

The most rapid degradation of pigments occurs during sinking, with exposure to high irradiance, temperature, and oxygen (Louda et al. 1998, 2002) and grazing and microbial processing (Cuddington and Leavitt 1999). In studies of lake sediments, it has been shown that epoxide-containing pigments, such as fucoxanthin, undergo rapid degradation compared with minimally substituted carotenoids such as β , β -

¹ Corresponding author (elie.verleyen@UGent.be).

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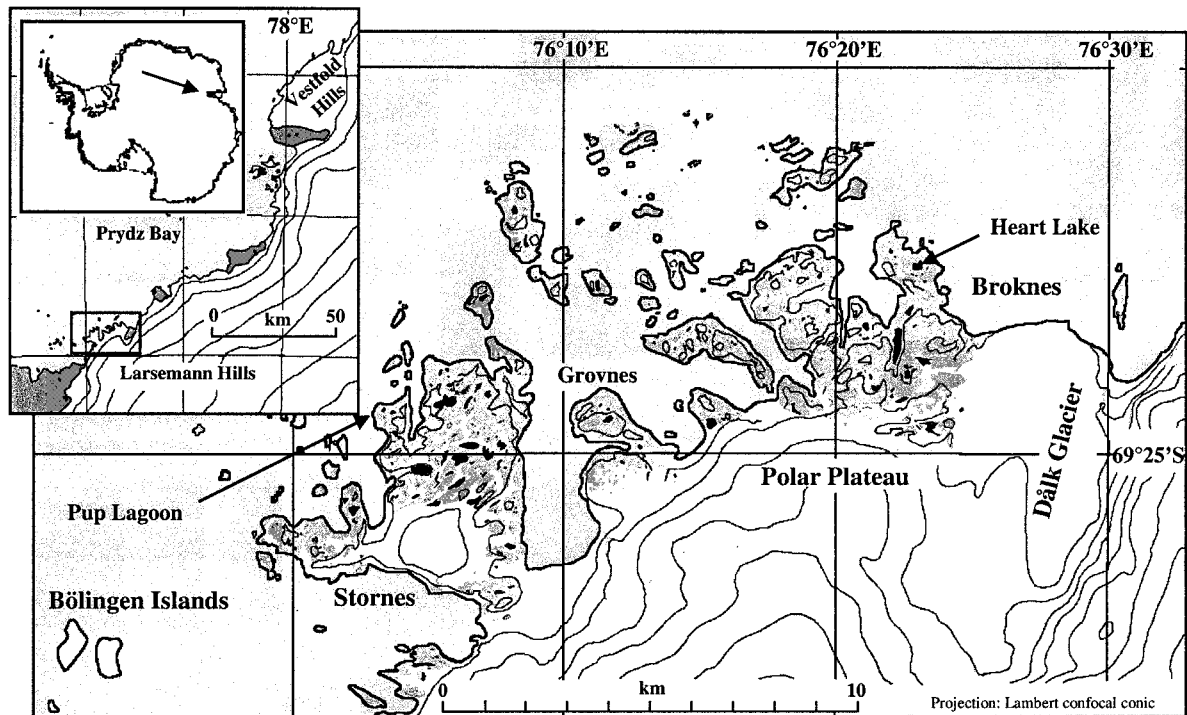


Fig. 1. Map of the Larsemann Hills, East Antarctica, showing the location of Pup Lagoon and Heart Lake. Lakes are indicated in black, ice-free areas in dark grey.

carotene and zeaxanthin (Leavitt et al. 1999). Consequently, many investigators feel that the best way to assess the accuracy of pigments as proxies of algal production is to compare changes in pigment composition of sediments with long-term ecological data sets that span the same time period (e.g., Leavitt and Findlay 1994; Leavitt et al. 1999; Bianchi et al. 2002b). Until now however, there has been no direct validation of pigments as biomarkers over longer timescales (more than centuries).

The aims of this study were twofold. First, we evaluated the preservation of fossil pigments and diatoms by comparing changes in biomarker concentrations with estimates of absolute diatom abundance (as cellular biovolume) in sediment cores from two East Antarctic lakes. Second, by combining fossil diatom and pigment data, we partitioned diatom production between benthic and sea ice or water column habitats, or both, during the marine and freshwater phases of ecosystem existence ($\sim 10,000$ yr before the present [BP] to the present). Furthermore, we propose that pigment:biovolume ratios can be used in both neo- and paleoecological studies to quantitatively evaluate recent and past ecosystem changes in marine and lacustrine environments.

Methods

Site description—The Larsemann Hills oasis, East Antarctica ($69^{\circ}23'S$, $76^{\circ}10'E$) comprises two main peninsulas and a number of offshore islands in Prydz Bay (Fig. 1). An extensive description of the geology, physiography, and climate of the region is given in Hodgson et al. (2001). There are a mixture of proglacial lakes and “isolation” lakes

formed by the isolation of marine bays during postglacial isostatic recovery. The latter contain marine sediments overlain by freshwater sediments. The lakes are ice covered for all but 2 or 3 months of summer. During this ice-free period, primary production is associated with benthic communities that experience high light intensities and UV radiation (UVR) stress (D. A. Hodgson unpubl. data). The benthic microbial mats are mainly composed of cyanobacteria, with green algae and diatoms as subdominants (Sabbe et al. 2004). Records of past microbial flora are archived in the stratigraphic sediment deposits in the bottom of the lakes. As one of only four major ice-free regions in East Antarctica, these stratigraphic sequences in the Larsemann Hills are being used as an important tool for understanding climate change, ice sheet extent, deglaciation history of the Antarctic coastline, and changes in the lacustrine and terrestrial environment (Squier et al. 2002; Verleyen et al. 2004a, 2004b).

Bulk sediment analyses—Sediment cores from two isolation lakes, Heart Lake and Pup Lagoon, were collected from the deepest part of each basin with the use of a combination of a Glew gravity corer for surface sediments and a modified Livingstone corer for deeper deposits. Cores were photographed, described for visible stratigraphy, sectioned in the field, and frozen until analysis. Every centimeter in the top 20 cm and every 5 cm between 20 cm and the bottom of the core were analyzed. Bulk sediment water content and dry mass were determined gravimetrically after drying for 24 h at $60^{\circ}C$.

Sediment samples from the Heart Lake ($n = 9$) and Pup Lagoon cores ($n = 8$) were dated with accelerator mass spec-

Table 1. Radiocarbon age, publication codes, corrected ages for the reservoir effect, and calibrated ages.

Depth (cm)	Conventional ^{14}C age (yr BP \pm SD)	Publication code	Corrected ^{14}C age (yr BP)	Calibrated age (yr BP)
Pup Lagoon				
0	Modern	AA-35718	—	Modern
20	675 \pm 40	AA-35748	—	653
50	1,270 \pm 40	AA-35749	—	1,204
100	1,590 \pm 45	AA-35750	—	1,517
150	2,150 \pm 45	AA-35751	—	2,139
200	3,915 \pm 45	AA-35752	2,615	2,749
250	6,085 \pm 50	AA-35753	4,785	5,504
300–302	6,380 \pm 50	CAMS-50377	5,080	5,794
Heart Lake				
0	Modern	AA-35716	—	Modern
20	2,620 \pm 45	AA-35736	—	2,750
105	6,795 \pm 55	AA-35737	5,495	6,290
175	7,110 \pm 55	AA-35738	5,810	6,639
245	8,070 \pm 75	AA-35739	—	9,009
275	8,508 \pm 59	AA-41164	—	9,504
280	21,780 \pm 160	AA-35740	—	—
320	25,460 \pm 230	AA-35741	—	—
360	10,314 \pm 65	AA-41633	9,014	10,207

trometry (AMS) ^{14}C by the U.K. Natural Environment Research Council Radiocarbon Laboratory (Table 1; Hodgson et al. 2001). Radiocarbon dates in both marine and lacustrine sections of the cores are reported as conventional radiocarbon years BP (relative to A.D. 1950) and were calibrated with the use of the atmospheric (terrestrial) decadal data set in the CALIB 4.3 program. A reservoir correction was applied to the radiocarbon dates derived from the marine samples by subtracting 1,300 yr, following recent conventions for the Southern Ocean. No reservoir correction was applied to dates from lacustrine sediments, because surface sediment dates indicate that ^{14}C in modern freshwater lakes in the Larsemann Hills is in near equilibrium with modern atmospheric CO_2 (Hodgson et al. 2001). In order to interpolate the ages of different layers in the cores, a linear sedimentation rate model was used.

Microfossils—Sediments for diatom analysis were digested with H_2O_2 (30%) and CH_3COOH (95%), and a standard solution of microspheres (Battarbee and Kneen 1982) was added to allow quantitative estimates of frustule concentration. Cleaned frustules were mounted on slides with Naphrax, and at least 400 valves or stomatocysts were counted in each sample. Identification of the diatom species was mainly based on Sabbe et al. (2003) and references therein. Communities from both cores were divided into zones following standard ordination and cluster analyses on the basis of total relative abundances of diatoms (Verleyen et al. 2004a, 2004b). The surface area (μm^2) of each diatom species was calculated with BIOVOL ver. 2.1 software (Kirschel 1996) on the basis of at least five measurements of the width and length of the frustules. Because the height of most frustules was difficult to measure, the surface area was used as an approximation for biovolume. Total diatom biovolume (TDB; Table 2) in each sample was calculated by

multiplying the absolute valve concentration (g^{-1} dry weight) of each taxon by the surface area of its frustule and then adding together this data from all taxa.

To evaluate diatom dissolution, a dissolution index (% dissolution, Table 2) was calculated following the morphological index of Ryves et al. (2001). This index, assessed microscopically, expresses the ratio between the number of diatoms with visible signs of dissolution and the total number of counted valves, which exceeded 50 in each sample.

Pigments—Algal pigments were extracted from bulk sediments following standard protocols described in Leavitt and Hodgson (2001) and Squier et al. (2002). All compounds were separated and quantified by high-performance liquid chromatography (HPLC) methods with a Kromasystem 2000 HPLC system and a Kontron pump, auto sampler, diode array detector, and reversed-phase Spherisorb ODS-2 column (25 cm \times 4.6 mm, 5- μm particle size) protected by a Phenomenex Guard cartridge (ODS2; 3 \times 4.6 mm; 3 μm). The 30-min gradient elution program, with a solvent system comprising methanol, ammonium acetate, acetonitrile and ethyl acetate, is described elsewhere (method B, Wright et al. 1991). The HPLC system was calibrated with the use of authentic pigment standards from the U.S. Environmental Protection Agency and compounds isolated from reference cultures following Scientific Committee on Oceanic Research (SCOR) protocols (Jeffrey et al. 1997). Chlorophylls and carotenoids were expressed as organic matter-specific concentrations (ng g^{-1} total organic carbon), because comparison of long-term plankton data with varved fossil records indicates that this metric most accurately captures variations in algal abundance (Leavitt and Findlay 1994). Furthermore, pigment and frustule concentrations were divided by the number of years of accumulation in each sediment interval to allow estimates of algal production. The taxonomic affin-

Table 2. Summary of the proxies employed in this study.

Code	Measure	Method	Indication
TDB	Total diatom biovolume=absolute diatom abundance* multiplied by frustule surface area†	Microscopy	Diatom production
TChla	Total Chl <i>a</i> =sum of Chl <i>a</i> (and its derivatives) and bacteriochlorophylls	Pigment analyses	Primary production of photosynthetic algae
TCD	Total diatom carotenoids=sum of fucoxanthin (and its derivatives), diatoxanthin, and diadinoxanthin	Pigment analyses	Diatom production
TDB/TChla	Total diatom biovolume/total Chl <i>a</i>	Microscopy and pigment analyses	Diatom production in relation to primary production
TCD/TChla	Total diatom carotenoids/total Chl <i>a</i>	Pigment analyses	Diatom production in relation to primary production
DD	Diadinoxanthin	Pigment analyses	
DT	Diatoxanthin	Pigment analyses	
(DD+DT)/TChla	Sum of diadinoxanthin and diatoxanthin divided by total Chl <i>a</i>	Pigment analyses	Mean irradiance of diatoms‡
Bcar/TChla	Sum of β -carotene/total Chl <i>a</i>	Pigment analyses	Mean irradiance of all algal groups
% diatom dissolution	Number of valves affected by dissolution as portion of total counted valves	Microscopy§	Amount of diatom dissolution
TFuc _{benthic} /TChla	Total fucoxanthin multiplied by relative abundance of benthic diatoms divided by total Chl <i>a</i>	Microscopy and pigment analyses	Benthic diatom production in relation to primary production
TFuc _{planktonic} /TChla	Total fucoxanthin multiplied by relative abundance of planktonic diatoms divided by total Chl <i>a</i>	Microscopy and pigment analyses	Planktonic diatom production in relation to primary production
TDB _{benthic} /TChla	Total diatom biomass of benthic taxa divided by total Chl <i>a</i>	Microscopy	Benthic diatom production in relation to primary production
TDB _{planktonic} /TChla	Total diatom biomass of planktonic taxa divided by total Chl <i>a</i>	Microscopy	Planktonic diatom production in relation to primary production

* Battarbee and Kneen (1982).

† Kirschtel (1996).

‡ Sigleo et al. (2001).

§ Ryves et al. (2001).

ities of the pigments were derived from Jeffrey et al. (1997) and Leavitt and Hodgson (2001) and are summarized in Table 3.

We estimated the total production of photosynthetic organisms as total chlorophyll (TChla) by calculating the sum of bacteriochlorophylls, chlorophyll *a* (Chl *a*), and their derivatives (e.g., chlorophyllide *a*, phaeophytin *a*, pyropheophytin *a*, phaeophorbide *a*, chlorins, and purpurin; Table 2). Total diatom carotenoid concentration (TDC; Table 2) was estimated as the sum of the diatom biomarkers fucoxanthin (and its derivatives), diatoxanthin (DT), and diadinoxanthin (DD). TDC/TChla and TDB/TChla were used to compare the pigment-based and microfossil-based estimates of diatom production (Table 2).

To assess the influence of light on the preservation conditions for pigments, two indicators of mean irradiance were calculated. These were based on ratios of the sum of the xanthophylls, (diadinoxanthin + diatoxanthin)/TChla, and the carotenoid β -carotene (Bcar), Bcar/TChla, which have previously been shown to indicate irradiance conditions experienced by diatoms and all algal groups, respectively (Table 2; Sigleo et al. 2000).

A first estimate of the proportion of diatom production in benthic and planktonic or sea ice habitats was calculated by multiplying the total fucoxanthin (TFuc; Table 2) content by the relative abundance of the benthic or planktonic diatom species. Although fucoxanthin is also found in brown seaweeds, these algae were rare at our sites, and we assume that fucoxanthin mainly records changes in diatom production. In this estimate, tycho planktonic taxa were assumed to be benthic during the lacustrine core sections, whereas sea ice and marginal ice edge diatoms (e.g., *Fragilariopsis* species) and chrysophyte cysts in the marine core levels were treated as planktonic taxa. A second estimate of the proportion of diatom production in benthic and planktonic or sea ice habitats (on the basis of diatom analyses alone) was calculated as the TDB in each habitat, according to procedures described above. In order to estimate changes in the contribution of diatoms to total primary production, each measure of the total diatom production was further divided by TChla to obtain a measure that is independent of the sedimentation rate.

Statistical analyses—Statistical relationships among time series were explored with basic time series procedures in

Table 3. The different pigments identified in the cores and their stability, affinity, and local interpretation. Relative degree of chemical stability and preservation is ranked from most (1) to least (4) stable on the basis of mesocosm experiments and mass balance studies (see Leavitt 1993). —, uncertain stability.

Pigment	Stability	Affinity	Interpretation
Chlorophyll			
Chlorophyll <i>a</i>	3	All photosynthetic algae	Relative production
Chlorophyllide <i>a</i>	—	Chl <i>a</i> derivative	Relative production
Phaeophytin <i>a</i>	1	Chl <i>a</i> derivative	Relative production
Phaeophorbide <i>a</i>	3	Chl <i>a</i> derivative	Relative production
Purpurin	—	Chl <i>a</i> derivative	Relative production
Pyropheophytin <i>a</i>	—	Chl <i>a</i> derivative	Relative production
Chlorin	—	Chl <i>a</i> derivative	Relative production
Carotenoid			
Fuxocanthin	2	Bacillariophyta, Prymnesiophyta, brown seaweeds, Raphidophyta, some Dinophyta with endosymbionts, Chrysophyta	Diatom production
Diadinoxanthin	3	Bacillariophyta, Prymnesiophyta, Dinophyta, Chrysophyta	Diatoms, measure for irradiance
Diatoxanthin	2	Bacillariophyta, Dinophyta, Chrysophyta	Diatoms, measure for irradiance
β -Carotene	1	All photosynthetic algae	Measure for irradiance

SYSTAT v. 10 software (SPSS). Preliminary analyses indicated that all predictor and response variables at both sites were not normally distributed and exhibited substantial temporal autocorrelations. Consequently, all variables were transformed sequentially by $\log(X + 1)$ and first difference transformations to normalize variance and remove autocorrelations. Cross-correlation analyses indicated that only lag = 0 correlations were significant and substantial. Therefore, we report these correlations as Pearson correlation coefficients for transformed variables. Similar procedures were used for correlation analyses of indices in freshwater and marine sections. Sediment samples 2–5 cm either side of the marine–freshwater transitions were eliminated from the analyses because they could not be clearly identified as exclusively marine or freshwater on the basis of diatom species identifications.

Results

Pup Lagoon—Diatom assemblages: On the basis of fossil diatom assemblages, the Pup Lagoon sediment core can be divided into three zones spanning the past ~5,800 yr (Figs. 2, 3). First, a marine zone between 302 and 150 cm (~5,800–2,140 yr BP, calibrated [cal.]) is characterized by marine- and sea ice-associated diatoms. Second, a well-marked transition zone from marine to freshwater conditions between 150 and 140 cm (~2,140–2,000 cal. yr BP) is characterized by stomatocysts from Chrysophyceae and lacustrine brackish water diatoms. Third, a freshwater zone between 140 cm and the top of the core (~2,000 cal. yr BP to present) is characterized by lacustrine freshwater and brackish water diatoms.

Past production: total diatom biovolume and biomarkers: Both morphological and biogeochemical proxies for past diatom production (TDB and TDC, Table 2) showed higher values in the marine core section than during the lacustrine

period (Fig. 2a). Following correction of time series for temporal autocorrelation, statistical analyses revealed that TDB and TDC were more strongly correlated in the marine interval ($r^2 = 0.358$, $p < 0.0001$) compared with the lacustrine period ($r^2 = 0.223$, $p = 0.001$; Table 4). TDB/TChla declined less than TDC/TChla during the transition from the marine to the lacustrine interval (Fig. 2b). Overall, average TDB/TDC was thus 4.4 times lower in the marine core section compared with the lacustrine period.

The first irradiation index ($[DD + DT]/TChla$; Table 2) was higher in the marine interval with lower and occasionally zero values in the lacustrine core section (Fig. 2c). In contrast, the second irradiation index, $Bcar/TChla$ (Table 2), was highly variable in both sections (Fig. 2c). In the marine interval, diatom dissolution was minimal, whereas it was relatively high during the lacustrine period (Fig. 3a).

Benthic diatom production was greater in the lacustrine core section than in the marine interval. In contrast, diatom production in the marine zone was dominated by sea ice and open-water assemblages (Fig. 3b,c). In the lacustrine interval a few allochthonous planktonic diatoms were present (blown in by sea spray); otherwise, there was no autochthonous freshwater planktonic flora. The difference between benthic and planktonic diatom production in the marine sections was higher with the use of the biovolume-based index (TDB) than with the pigment-based (relative abundance) index (TFuc).

Heart Lake—Diatom assemblages: On the basis of fossil diatom assemblages, the Heart Lake sediment core can be divided into five zones spanning the past ~10,000 years (Figs. 4, 5). First, a marine zone between 361 and 355 cm (~10,215–10,166 cal. yr BP) was characterized by marine diatoms. Second, a glacial till and diamicton zone between 355 and 275 cm (~10,166–9504 cal. yr BP) contained only rare and fragmented diatoms. (As a consequence, pigment data from this part of the core were not included in statistical

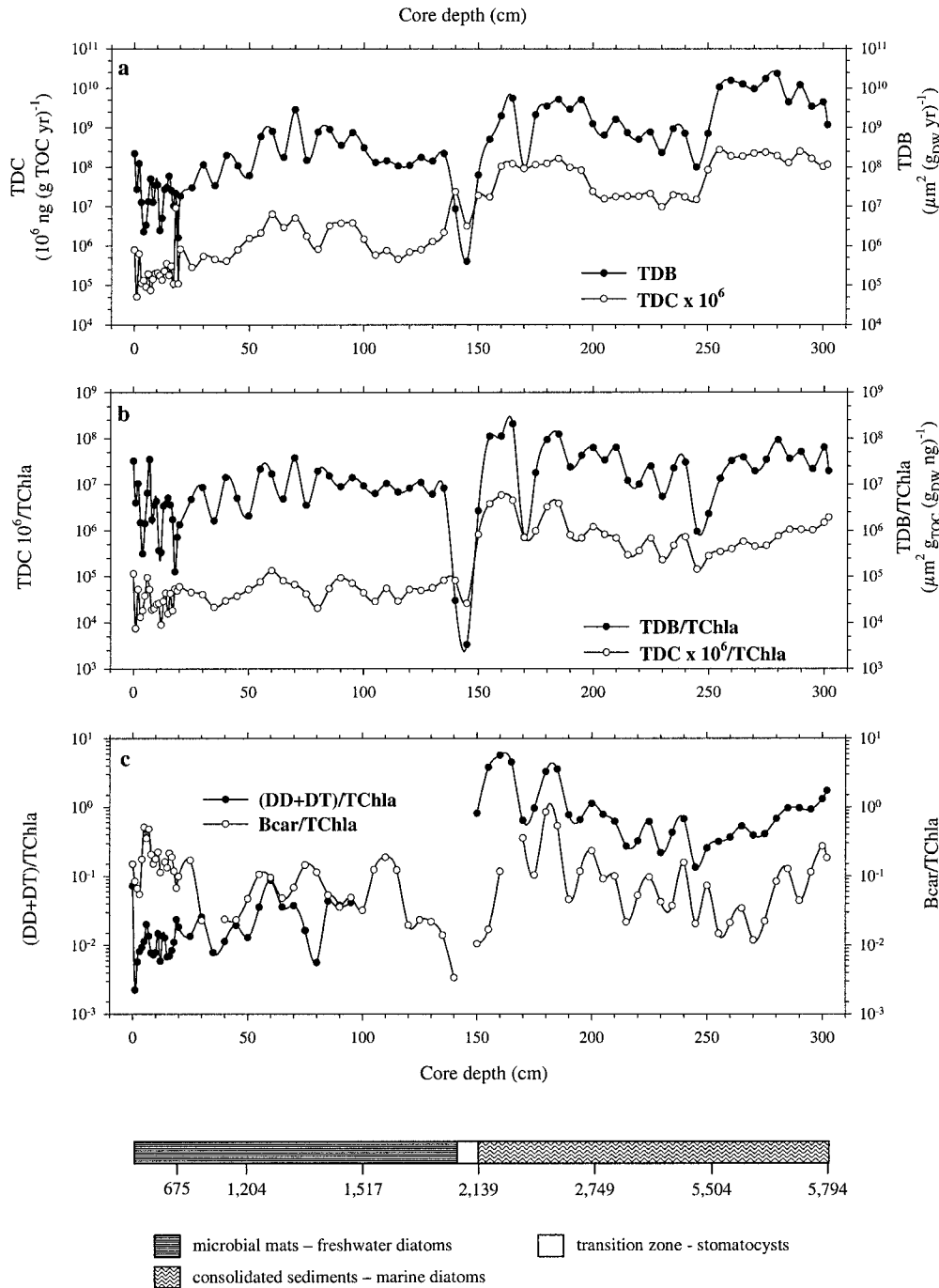


Fig. 2. Proxy reconstructions of environmental changes in Pup Lagoon. (a) Total diatom biovolume (TDB) and total screening pigments for diatoms (TDC; Table 2). (b) Total diatom biovolume divided by total Chl *a* (TDB/TChla) and total diatom carotenoids divided by total Chl *a* (TDC/TChla). (c) Sum of diadinoxanthin and diatoxanthin divided by total Chl *a* ([DD + DT]/TChla) and β -carotene divided by total Chl *a* (Bcar/TChla).

analyses.) Third, a freshwater zone between 275 and 245 cm (~9,504–9,009 cal. yr BP) was characterized mainly by lacustrine diatoms, except at 262 cm where marine diatoms were abundant and at 270 cm where lacustrine and marine diatoms co-occurred. Fourth, another marine zone between 245 and 25 cm (~9,009–2,958 cal. yr BP) contained marine diatoms. Fifth, a freshwater zone between 25 and 0 cm (~2,958 cal. yr BP to present) contained lacustrine diatoms.

Past production: total diatom biovolume and biomarkers: TDB concentrations remained relatively constant throughout the core (Fig. 4a). In contrast, TDC values were extremely low in the lacustrine intervals and led to a greater variation in TDC/TChla between marine and lacustrine sections than that recorded for TDB/TChla (Fig. 4b). Both morphological and biogeochemical proxies for past diatom production (TDB and TDC) were positively correlated throughout the

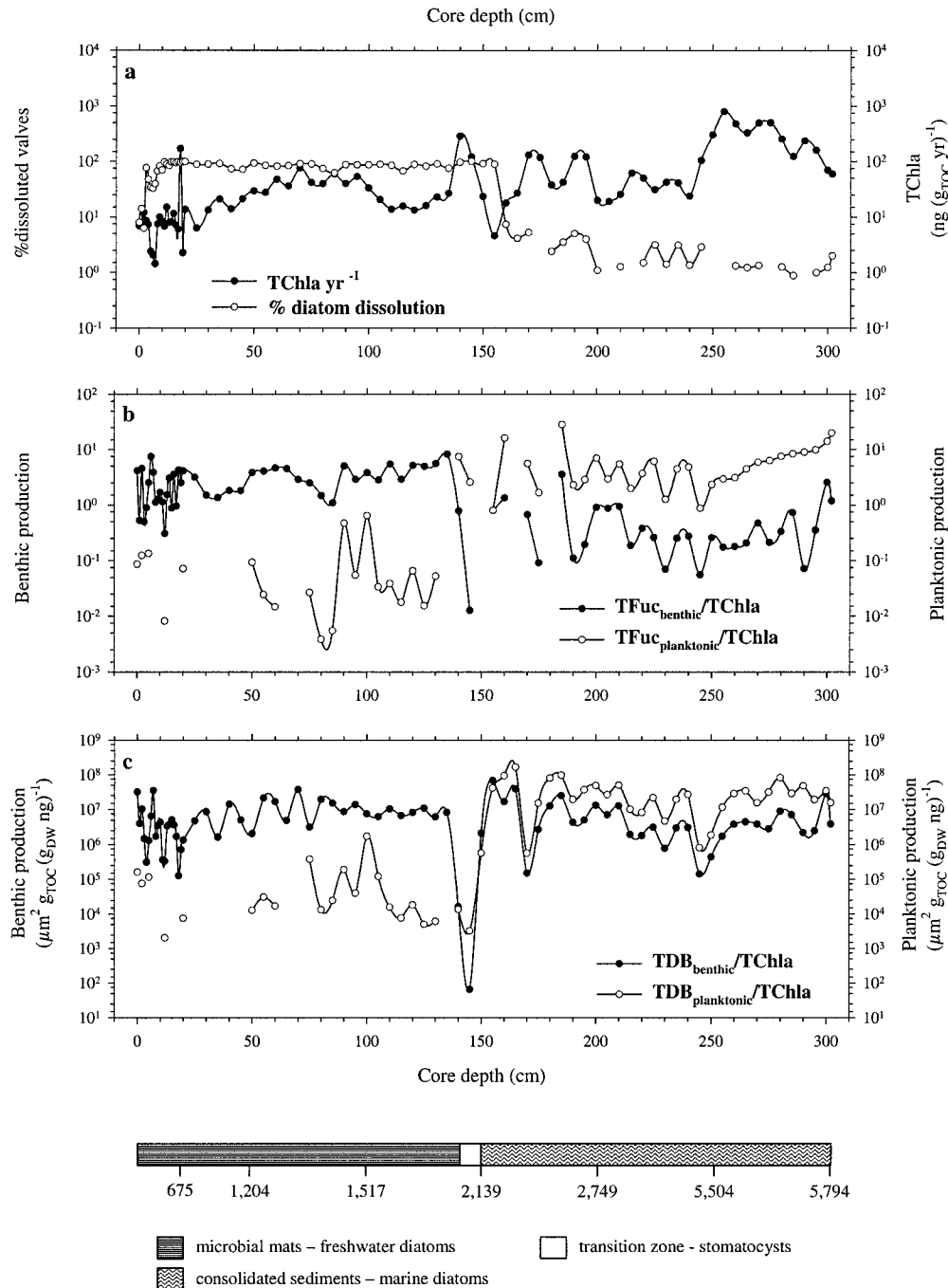


Fig. 3. Proxy reconstructions of environmental changes in Pup Lagoon. (a) Percentage of valves with visible signs of dissolution out of total counted valves and total Chl *a* per year (TChla yr⁻¹). (b) Water column and sea ice (TFuc_{planktonic}/TChla) and benthic (TFuc_{benthic}/TChla) diatom production relative to total primary production on the basis of total fucoxanthin content and proportion of benthic taxa. (c) Water column and sea ice (TDB_{planktonic}/TChla) and benthic (TDB_{benthic}/TChla) diatom production relative to total primary production on the basis of absolute diatom counts, biovolume measurements, and proportion of benthic taxa. Zoning is based on diatom data and macroscopic lithological observations in the field (Verleyen et al. 2004a).

entire core ($r^2 = 0.187$, $p < 0.0001$; Table 4); however, correlations were highly significant in the marine intervals ($r^2 = 0.557$, $p < 0.0001$) but not in the lacustrine core sections ($r^2 = 0.102$, $p = 0.111$; Table 4). Average TDB/TDC was thus 32.2 times lower during the marine period compared with the lacustrine interval.

The first irradiance index ($[DD + DT]/TChla$) was low in the lacustrine zones and higher in the marine intervals. In contrast, the second irradiance index ($Bcar/TChla$) showed no clear differences in value between marine and lacustrine sections (Fig. 4c). As in the Pup Lagoon core, diatom dissolution was relatively high in the lacustrine zones and low

Table 4. Correlation statistics (correlation coefficient, p value and number of cases [n]) between the diatom production proxies TDB and TDC in different zones in the Pup Lagoon (PL) and Heart Lake (HL) cores.

	r^2	p	n
PL			
Lacustrine	0.223	=0.001	44
Marine	0.358	<0.0001	31
Entire core	0.227	<0.0001	77
HL			
Lacustrine	0.102	=0.111	27
Marine	0.557	<0.0001	44
Entire core	0.187	<0.0001	88

or even zero (i.e., no visible signs of dissolution) in the marine sections (Fig. 5a).

Similar to Pup Lagoon, benthic diatom production was greater in the lacustrine zones than in the marine intervals, where diatoms were mainly situated in sea ice and open-water habitats (Fig. 5b,c). Differences between benthic and planktonic diatom production were also higher when using the pigment-based index (TFuc/TChla) than when using the biovolume-based index (TDB/TChla) (Fig. 5c).

Discussion

Although pigments are widely used in paleolimnology (see Leavitt and Hodgson 2001 and references therein), few attempts have been made to compare fossil pigments with alternative fossil proxies for algal production, particularly in marine environments. Recent comparisons of modern phytoplankton and sedimentary pigments in the Baltic Sea reveal a linear correlation between algal biomass accumulation and fossil concentration (Bianchi et al. 2002b). Similar correlations are found in freshwater environments (e.g., Leavitt and Findlay 1994; Leavitt et al. 1999). Unfortunately, analysis and interpretation of sedimentary pigments on millennial timescales is less straightforward, mainly because of a lack of information regarding long-term pigment stability. Here, we compared absolute diatom counts with pigment-derived estimates of diatom production. In doing so, we were able to evaluate long-term changes in pigment, diatom preservation, or both in marine and freshwater sediments, and we were able to evaluate the relative influence of the different preservation environments (cf. Leavitt 1993; Bianchi et al. 2002b).

In both lakes, TDC/TDB were higher in the marine zones compared with the lacustrine zones (Figs. 2, 4). The difference in the pigment-based (TDB/TChla) and biovolume-based (TDC/TChla) ratio (and thus TDB/TDC) between these contrasting environments might arise from variations in diatom dissolution, cellular pigment quotas, physiological response to significantly altered light regimes, pigment preservation, or a combination of factors.

The diatom dissolution index was relatively high in the lacustrine intervals, implying that changes in diatom preservation could be partially responsible for the lack of correlation between the pigment-based and biovolume-based

measures of diatom production in the lacustrine sections. This was probably related to the pore waters being undersaturated in SiO_2 (Ryves et al. 2001). In contrast, diatom dissolution was extremely low and often nearly absent in the marine zones, which is in agreement with previous studies of anoxic marine basins in East Antarctica (McMinn 1995). Diatom dissolution in the lacustrine zones, however, cannot account for the 4- and 32-fold increases in average TDB/TDC when moving from the marine to lacustrine sections in the Pup Lagoon and Heart Lake cores, respectively.

Although changes in cellular pigment quotas are difficult to assess, it is unlikely that they can explain the total absence of diatoxanthin and diadinoxanthin in some core sections of the Pup Lagoon core (Fig. 2c). Also, physiological response to altered light regimes could not have produced the large changes in pigment:biovolume ratios because one of our irradiance indices (Bcar/TChla, Figs. 2c, 4c) shows little variation between marine and freshwater zones, suggesting a more or less constant light regime. In contrast, the other irradiance index ($(\text{DD} + \text{DT})/\text{TChla}$) is more variable and even zero in some lacustrine core levels, but this is probably related to differential pigment preservation between marine and freshwater zones rather than changes in the light environment.

Pigment preservation, was then, apparently better in the marine sections than in the freshwater zones of both lakes. In general, pigment preservation is reduced by prolonged exposure to elevated oxygen concentration or high irradiance, temperature, grazing or microbial processing (Louda et al. 1998, 2002; Cuddington and Leavitt 1999; Leavitt and Hodgson 2001). We therefore speculate that improved preservation in marine sediments might have arisen as a result of anoxia under sea ice (cf. McMinn 1995). In support of this hypothesis, we note that bacteriochlorophylls were abundant in the marine intervals of the Pup Lagoon core, but not during freshwater episodes (Verleyen et al. 2004a). Such bacteriochlorophylls are produced by obligate anaerobic sulfur bacteria. In contrast, oxygen concentrations have been shown to reach 120–170% of air equilibrium values in the upper 5 mm of microbial mats in freshwater systems near McMurdo Sound (Vincent et al. 1993), thereby leading to selective degradation of pigments, as is seen in many temperate lakes (Leavitt 1993). Together, these patterns suggest that pigment preservation (and diatom dissolution) could vary substantially between marine and lacustrine sedimentary environments in Antarctica and that photoprotective compounds, such as diadinoxanthin and diatoxanthin, need to be used with caution if they are to be used as a quantitative measure of the contribution of diatoms to primary production or as measures of irradiance. Fucoxanthin was unexpectedly much better preserved than either diatoxanthin or diadinoxanthin, even though the former compound is known to be chemically unstable (Leavitt 1993). However, this remarkable preservation of fucoxanthin is in good agreement with recent results from the Scotia Sea (Sigleo et al. 2000) and the Baltic Sea proper (Bianchi et al. 2002b). In the latter study, fucoxanthin was shown to be highly correlated with diatom biomass averaged over 5 yr (to account for sediment redistribution). Clearly, more research concerning pigment

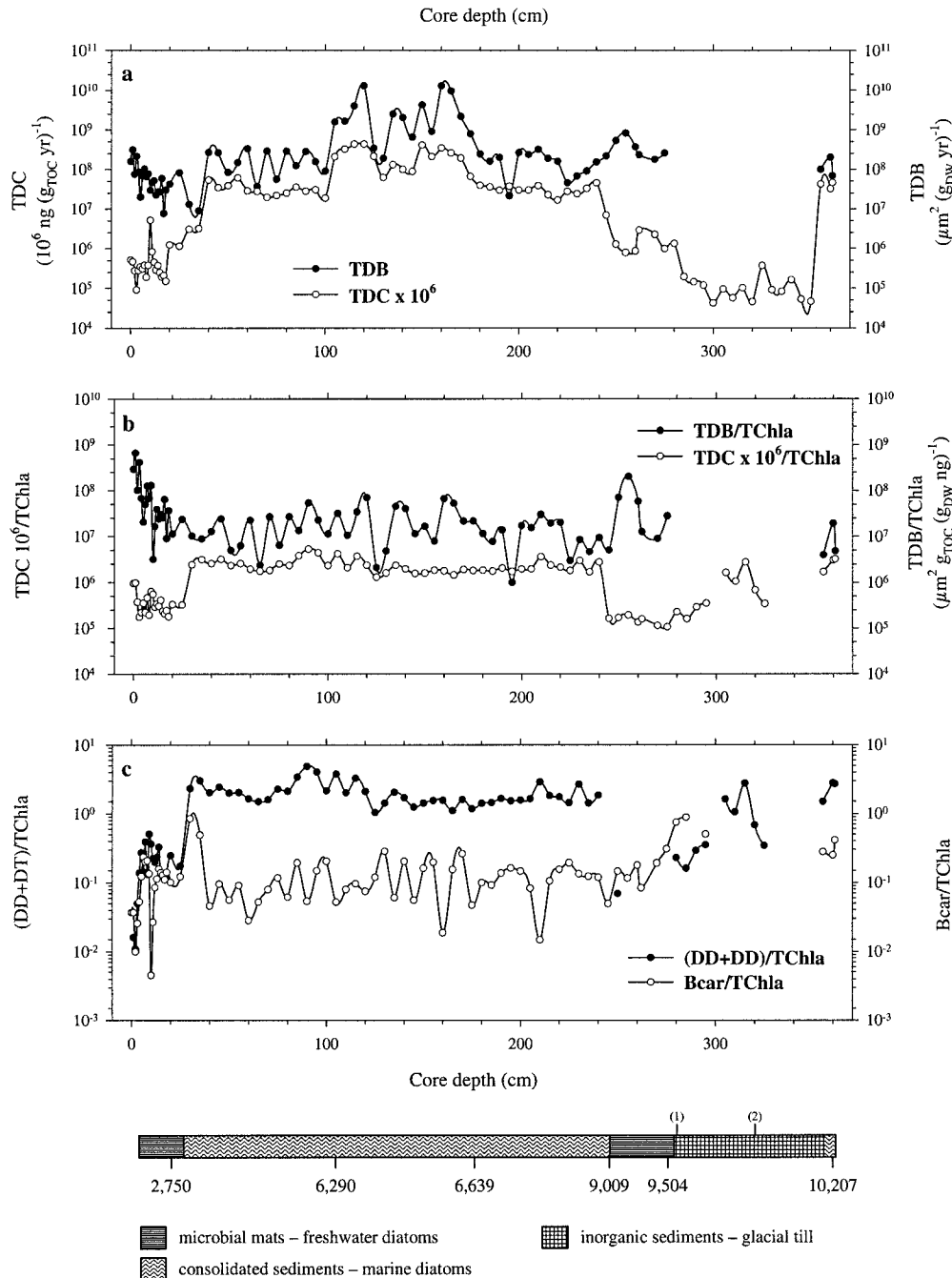


Fig. 4. Proxy reconstructions of environmental changes in Heart Lake. (a) Total diatom biovolume (TDB) and total screening pigments for diatoms (TDC, Table 2). (b) Total diatom biovolume divided by total Chl *a* (TDB/TChl*a*) and total diatom carotenoids divided by total Chl *a* (TDC/TChl*a*). (c) Sum of diadinoxanthin and diatoxanthin divided by total Chl *a* [(DD + DT)/TChl*a*] and β -carotene divided by total Chl *a* (Bcar/TChl*a*).

stability and preservation in different sedimentary environments is needed.

We suggest that the combination of pigment and diatom biovolume estimates is a useful tool for distinguishing historical trends arising from production and preservation artifacts during ecosystem changes (e.g., Cuddington and Leavitt 1999), which is a key goal of many paleoecological studies (e.g., Leavitt and Hodgson 2001, Hodgson et al.

2003). In particular, use of a proxy ratio will be informative in cases where diatom preservation is poor, such as that recorded in Lake Baikal (Ryves et al. 2003) and in some saline lakes (Ryves et al. 2001) or in cases where pigment preservation is poor (e.g., Hurley and Armstrong 1991).

The use of both pigment and frustule biovolume estimates of diatom abundance also allowed us to partition diatom production among habitats, as well as determine how these dif-

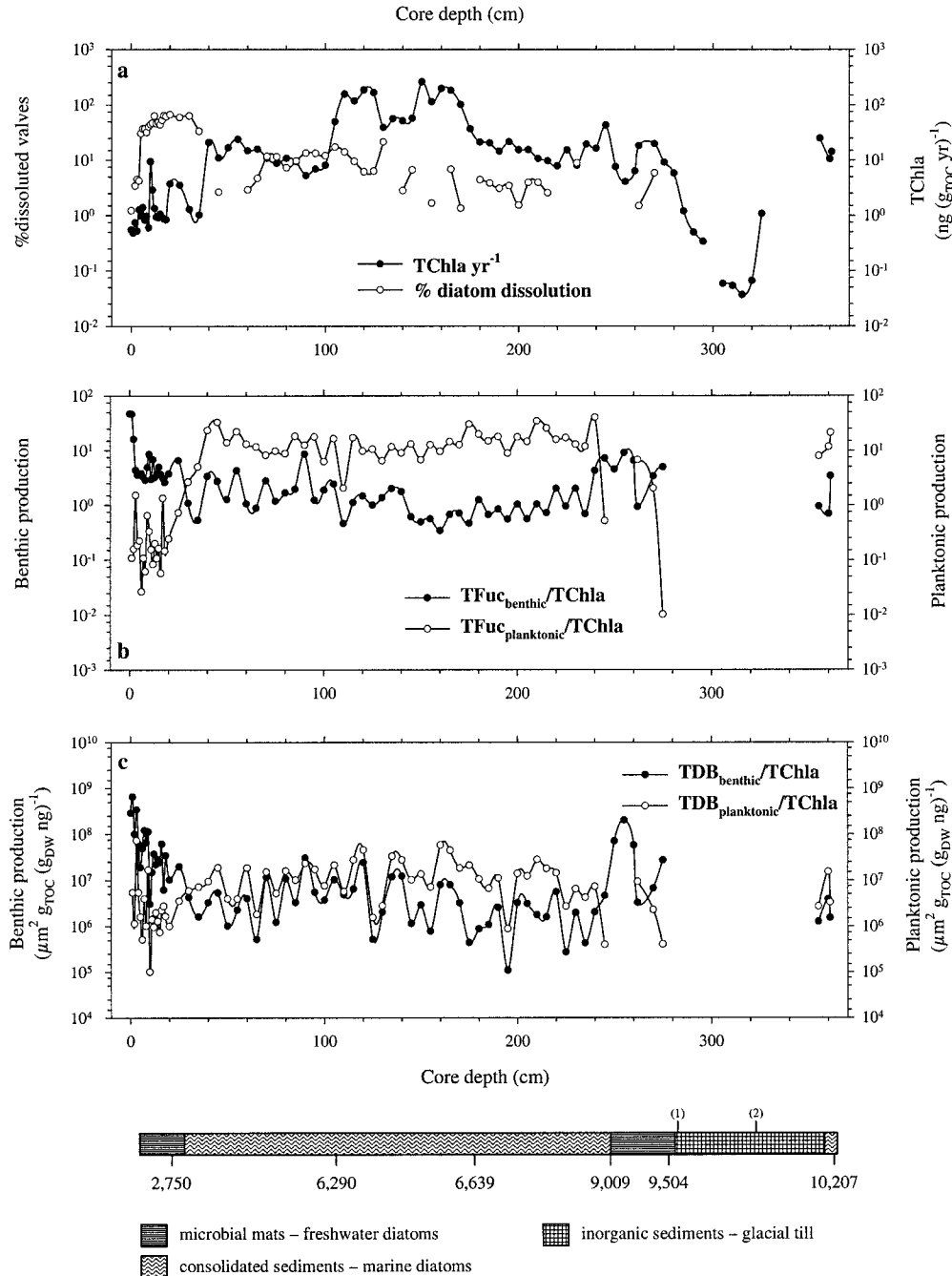


Fig. 5. Proxy reconstructions of environmental changes in Heart Lake. (a) Percentage of valves with visible signs of dissolution out of total counted valves and total Chl *a* per year (TChl a yr^{-1}). (b) Water column and sea ice (TFuc_{planktonic}/TChl a) and benthic (TFuc_{benthic}/TChl a) diatom production relative to total primary production on the basis of total fucoxanthin content and proportion of benthic taxa. (c) Water column and sea ice (TDB_{planktonic}/TChl a) and benthic (TDB_{benthic}/TChl a) diatom production relative to total primary production on the basis of absolute diatom counts, biovolume measurements, and proportion of benthic taxa. Zoning is based on diatom data and macroscopic lithological observations in the field. Radiocarbon dates in the washed-in glacial till zone at 280 cm⁽¹⁾ and 320 cm⁽²⁾ are 21,780 and 25,460 yr BP, respectively, and not calibrated (*see* Verleyen et al. 2004b for a detailed discussion).

ferences varied as a function of ecosystem state (marine, freshwater), which is certainly not accomplished when pigments are used alone. Overall, we found that transitions from marine (primarily planktonic and sea ice) to freshwater (primarily benthic) habitats were accompanied by a 2-fold de-

cline in diatom production in the Pup Lagoon core and a 26-fold decline in the Heart Lake core if the pigment-derived proxy was used (TFuc/TChl a , Table 2) and that these declines are not entirely compensated by increased production of benthic taxa in the freshwater environment (Figs. 3b,c,

5b,c). These results are in good agreement with previous studies in Arctic and Antarctic ultraoligotrophic freshwater lakes in polar deserts, where diatom production is almost exclusively associated with benthic habitats (e.g., Sabbe et al. 2004), but can be quite high (Vadeboncoeur et al. 2003) and with marine studies that show high diatom production in the ice edge zone (e.g., Brzezinski et al. 2001; Arrigo et al. 2003).

By combining diatom biovolumes with pigment analyses, one can therefore obtain an independent reference needed to assess the relative degree of preservation of both biogeochemical and morphological fossils. Such information is essential in paleoecological reconstructions involving past ecosystem production and in reducing errors associated with changes in the physical structure of ecosystems that control changes in fossil pigment deposition and preservation. Alternatively, changes in pigment preservation relative to information from diatom frustules may be used to document changes in the mixing regimes of lakes, as well as the relative importance of different algal classes to total primary production (Leavitt 1993). In addition, by partitioning fucoxanthin content and total diatom biomass among benthic and planktonic or sea ice diatoms, we were able to differentiate diatom production in both marine and freshwater environments. Thus, in reconstructions of historical primary production and of the algal groups and habitats that contribute to it, a combined analysis of biogeochemical and morphological fossils might permit more accurate, reliable, and detailed interpretations in both paleo- and neocological research.

References

- ARRIGO, K. R., D. L. WORTHEN, AND D. H. ROBINSON. 2003. A coupled ocean–ecosystem model of the Ross Sea: 2. Iron regulation of phytoplankton taxonomic variability and primary production. *J. Geophys. Res., C* **108**. [doi: 10.1029/2001JC000856]
- BATTARBEE, R. W., AND M. J. KNEEN. 1982. The use of electronically counted microspheres in absolute diatom analysis. *Limnol. Oceanogr.* **27**: 184–188.
- BIANCHI, T. S., C. ROLFF, B. WIDBOM, AND R. ELMGREN. 2002a. Phytoplankton pigments in Baltic Sea seston and sediments: Seasonal variability, fluxes, and transformations. *Estuar. Coast. Shelf Sci.* **55**: 369–383.
- , AND OTHERS. 2002b. Do sediments from coastal sites accurately reflect time trends in water column phytoplankton? A test from Himmerfjorden Bay (Baltic Sea proper). *Limnol. Oceanogr.* **47**: 1537–1544.
- BRZEZINSKI, M. A., D. M. NELSON, V. M. FRANCK, AND D. E. SIGMON. 2001. Silicon dynamics within an intense open-ocean diatom bloom in the Pacific sector of the Southern Ocean. *Deep-Sea Res. II* **48**: 3997–4018.
- CUDDINGTON, K., AND P. R. LEAVITT. 1999. An individual-based model of pigment flux in lakes: Implications for organic biogeochemistry and paleoecology. *Can. J. Fish. Aquat. Sci.* **56**: 1964–1977.
- HODGSON, D. A., AND OTHERS. 2001. Were the Larsemann Hills ice-free through the last Glacial Maximum? *Antarct. Sci.* **13**: 440–454.
- , AND OTHERS. 2003. Colonisation, succession and extinction of marine floras during a glacial cycle—a case study from the Windmill Islands (East Antarctica) using biomarkers. *Paleoceanography* **18**: 1067. doi: 10.1029/2002PA000775.
- HURLEY, J. P., AND D. E. ARMSTRONG. 1991. Pigment preservation in lake sediments—a comparison of sedimentary environments in Trout Lake, Wisconsin. *Can. J. Fish. Aquat. Sci.* **48**: 472–486.
- JEFFREY, S. W., R. F. C. MANTOURA, AND T. BJØRNLAND. 1997. Data for the identification of 47 key phytoplankton pigments, p. 447–554. In S. W. Jeffrey, R. F. C. Mantoura, and S. W. Wright [eds.], *Phytoplankton pigments in oceanography, guidelines to modern methods*. UNESCO.
- KIRSCHTEL, D. B. 1996. BIOVOL Ver. 2.1. Available at: <http://www.msu.edu/~kirschte/biovol/index.html>. Accessed on 5 June 2003.
- LEAVITT, P. R. 1993. A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. *J. Paleolimnol.* **9**: 109–127.
- , AND D. L. FINDLAY. 1994. Comparison of fossil pigments with 20 years of phytoplankton data from eutrophic Lake 227, experimental lakes area, Ontario. *Can. J. Fish. Aquat. Sci.* **51**: 2286–2299.
- , AND D. A. HODGSON. 2001. Practical methods for analysis of sedimentary pigments, p. 295–325. In J. P. Smol and W. M. Last [eds.], *Developments in palaeoenvironmental research, v. 3: Tracking environmental changes using lake sediments, biological techniques and indicators*. Kluwer.
- , D. L. FINDLAY, R. I. HALL, AND J. P. SMOL. 1999. Algal responses to dissolved organic carbon loss and pH decline during whole-lake acidification: Evidence from paleolimnology. *Limnol. Oceanogr.* **44**: 757–773.
- LOUDA, J. W., J. LI, L. LIU, M. N. WINFREE, AND E. W. BAKER. 1998. Chlorophyll-*a* degradation during cellular senescence and death. *Org. Geochem.* **29**: 1233–1251.
- , L. LIU, AND E. W. BAKER. 2002. Senescence- and death-related alternation of chlorophylls and carotenoids in marine phytoplankton. *Org. Geochem.* **33**: 1635–1653.
- MACKEY, M. D., D. J. MACKEY, H. W. HIGGINS, AND S. W. WRIGHT. 1996. CHEMTAX—a program for estimating class abundances from chemical markers: Application to HPLC measurements of phytoplankton. *Mar. Ecol. Prog. Ser.* **144**: 265–283.
- MCMINN, A. 1995. Comparison of diatom preservation between oxic and anoxic basins in Ellis Fjord, Antarctica. *Diatom Res.* **10**: 145–151.
- RYVES, D. B., S. JUGGINS, S. C. FRITZ, AND R. W. BATTARBEE. 2001. Experimental diatom dissolution and the quantification of microfossil preservation in sediments. *Palaeogeogr. Palaeoclim. Palaeoceanogr.* **172**: 99–113.
- , D. H. JEWSON, M. STURM, R. W. BATTARBEE, R. J. FLOWER, A. W. MACKAY, AND N. G. GRANIN. 2003. Quantitative and qualitative relationships between planktonic diatom communities and diatom assemblages in sedimenting material and surface sediments in Lake Baikal, Siberia. *Limnol. Oceanogr.* **48**: 1643–1661.
- SABBE, K., E. VERLEYEN, D. A. HODGSON, K. VANHOUTTE, AND W. VYVERMAN. 2003. Benthic diatom flora of freshwater and saline lakes in the Larsemann Hills and Rauer Islands (E-Antarctica). *Antarct. Sci.* **15**: 227–248.
- , D. A. HODGSON, E. VERLEYEN, A. TATON, A. WILMOTTE, K. VANHOUTTE, AND W. VYVERMAN. 2004. Effects of physical disturbance and salinity on microbial mat structure and composition in continental Antarctic lakes (Larsemann Hills and Bøllingen Islands). *Freshw. Biol.* **49**: 296–319.
- SIGLEO, A. C., P. J. NEALE, AND A. M. SPECTOR. 2000. Phytoplankton pigments at the Weddell–Scotia confluence during the 1993 austral spring. *J. Plankton Res.* **22**: 1989–2006.
- SQUIER, A. H., D. A. HODGSON, AND B. J. KEELY. 2002. Sedimen-

- tary pigments as markers for environmental change in an Antarctic lake. *Org. Geochem.* **33**: 1655–1665.
- VADEBONCOEUR, Y., E. JEPPESEN, M. J. VANDER ZANDEN, H. H. SCHIERUP, K. CHRISTOFFERSEN, AND D. M. LODGE. 2003. From Greenland to green lakes: Cultural eutrophication and the loss of benthic pathways in lakes. *Limnol. Oceanogr.* **48**: 1408–1418.
- VERLEYEN, E., D. A. HODGSON, K. SABBE, K. VANHOUTTE, AND W. VYVERMAN. 2004a. Coastal oceanographic conditions in the Prydz Bay region (East Antarctica) during the Holocene recorded in an isolation basin. *Holocene* **14**: 246–257.
- , ———, ———, AND W. VYVERMAN. 2004b. Late Quaternary deglaciation and climate history of the Larsemann Hills (East Antarctica). *J. Quat. Sci.* **19**: 361–375.
- VERSCHUREN, D., C. COCQUYT, J. TIBBY, C. N. ROBERTS, AND P. R. LEAVITT. 1999. Long-term dynamics of algal and invertebrate communities in a small, fluctuating tropical soda lake. *Limnol. Oceanogr.* **44**: 1216–1231.
- VINCENT, W. F., R. W. CASTENHOLZ, M. T. DOWNES, AND C. HOWARD-WILLIAMS. 1993. Antarctic cyanobacteria: Light, nutrients, and photosynthesis in the microbial mat environment. *J. Phycol.* **29**: 745–755.
- WRIGHT, S. W., S. W. JEFFREY, R. F. C. MANTOURA, C. A. LLEWELLYN, T. BJØRNLAND, D. REPETA, AND N. A. WELSCHMEYER. 1991. Improved HPLC method for analysis of chlorophylls and carotenoids from marine phytoplankton. *Mar. Ecol. Prog. Ser.* **77**: 183–196.

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