CHAPTER EIGHT

DIATOMS: FROM MICROPALEONTOLOGY TO ISOTOPE GEOCHEMISTRY

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Contents

1. INTRODUCTION

1.1. Classification of Diatoms

Kingdom: Protista

Phylum: Chrysophyta

Class: Bacillariophyceae

Orders: Centrales and Pennales

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Diatoms are unicellular organisms in which the cell is encapsulated in an amorphous silica box, called the frustule, composed of two intricate valves. Diatom size varies from 2 μm to 1–2 mm, and diatom shape exhibits any variation from round (Centrales) to needle-like (Pennales). The frustule is highly ornamented with pores (areolae), processes (labiate, strutted, internal or external, with or without extensions), spines, costae, horns, hyaline areas, and other distinguishing features. Diatom taxonomy is historically based on the shape and ornamentation of the frustule (Pfitzer, 1871; Schütt, 1896; Simonsen, 1979; Round, Crawford, & Mann, 1990; Hasle & Syversten, 1997).

Centric diatoms are separated into three suborders, based on the presence or absence of the marginal ring of processes and the polarity of the symmetry, while Pennate diatoms are separated into two suborders based on the presence or absence of the raphe, observed as an elongated fissure or pair of fissures through the valve wall (Figure 1) (see Anonymous (1975) for more details on the distinguishing features of diatoms). Recently, molecular investigations provided a new understanding of species determination and showed that several species may share the

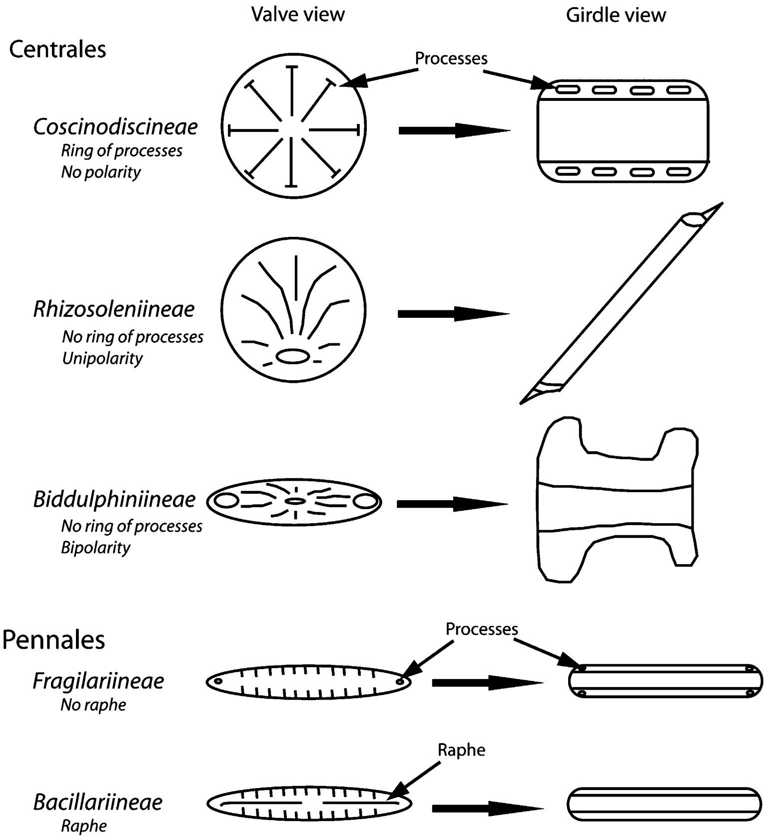


Figure 1 Schematic diagram of Centric and Pennate diatom sub-orders (redrawn with permission from Hasle & Syvertsen, 1997).

same morphology (Graham & Wilcox, 2000). The question of whether this genetic variability is related to environmental conditions and may be useful for paleoclimatic investigations is still under debate. To date, the classification system developed by Simonsen (1979) is still the most widely accepted.

1.2. Biology of Diatoms

Diatoms are photosynthetic organisms possessing yellow–brown chloroplasts with pigments including chlorophyll *a* and *c*, β-carothene, fucoxanthin, diatoxanthin, and diadinoxanthin (Jeffrey, Mantoura, & Wight, 1997). This large set of pigments enables diatoms to capture a wide range of wavelengths and to live at low light levels, for example under sea-ice that filters most of the solar energy.

Diatoms generally reproduce through vegetative fission at a rate of 0.1–8 times per day. This vegetative reproduction allows diatoms to build a very high biomass, which is at the origin of diatomite, when the preservation process allows it. Vegetative reproduction involves the formation of two new hypovalves in the parent diatom's frustule, which progressively reduce the average size of diatom frustules in the population. At a given threshold, diatoms undergo sexual reproduction through gamete fusion and the formation of an auxospore that renews a full-sized vegetative cell (Round, 1972). Some species have another peculiar reproductive stage, the resting spore. The spore is formed under unfavorable conditions (depleted nutrient levels, low light levels, etc.) and allows the diatom to survive until better conditions return.

1.3. Ecology of Diatoms

About 285 genera and 12,000 species of diatoms have been identified (Round et al., 1990). Diatoms are found in almost every aquatic environment, including fresh and marine waters. They are nonmotile and restricted to the photic zone. Diatoms may be solitary as well as colonial. In the marine environment diatoms are generally planktonic, although some benthic or pseudo-benthic species attached to macroalgae or sea-ice are also encountered.

The relationships between abiotic and biotic factors and diatom distribution in surface water are poorly understood. Many factors interact to determine the distribution of planktonic diatoms in any given oceanic region, but the most important factors are sea-surface temperatures (SSTs) (Neori & Holm-Hansen, 1982), sea-ice conditions (SIC) (Horner, 1985), macro- and micronutrient levels (Fitzwater, Coale, Gordon, Johnson, & Ondrusek, 1996), stability of the surface water layer (Leventer, 1991), light levels (El Sayed, 1990), and grazing (El Sayed, 1990). Salinity may also exert a major role on diatom distribution, especially in coastal regions and regions of the Artic Ocean influenced by sea-ice, where strong gradients in salinity exist (Campeau, Pienitz, & Héquette, 1998; Licursi, Sierra, & Gomez, 2006). Similarly, many factors interact to determine the distribution of benthic diatoms, the most important being the biotope category (Aleem, 1950), the substrate (Round et al., 1990), and the water depth (Campeau, Pienitz, & Héquette, 1999), perhaps associated with irradiance penetration. Benthic diatoms are generally restricted to environments shallower than 100 m.

In the world ocean, diatoms are restricted to cold, nutrient-rich regions where silicic acid is not limiting, such as in the polar regions, the coastal and equatorial upwelling systems, and in the coastal areas. In other regions, diatoms are outcompeted by carbonate organisms that have lower nutrient requirements.

Some diatom species thrive in very narrow ranges of conditions and are encountered in specific regions. For example, some *Fragilariopsis* species occur in both polar regions, while others occur only in upwelling systems. This specificity can be extreme and some diatoms are endemic to a single region. Several species are, for example, restricted to the Antarctic Ocean, such as *Fragilariopsis kerguelensis* and *F. curta*. Species thriving in a limited range of conditions are obviously much more useful than widely distributed species for paleoceanographic reconstructions. Although it is difficult to talk about diatom zonation for the world ocean, clear zonations are evident in specific areas. Different ecological preferences lead to gradients of different diatom species abundances in surface waters (Heiden & Kolbe, 1928; Hendey, 1937; Hustedt, 1958; Hasle, 1969) and generally in surface sediments (Sancetta, 1992; DeFelice & Wise, 1981; Abrantes, 1988a; Koç-Karpuz & Schrader, 1990; Armand, Crosta, Romero, & Pichon, 2005; Crosta, Romero, Armand, & Pichon, 2005a; Romero, Armand, Crosta, & Pichon, 2005). Understanding diatom ecology in the study area is therefore essential for paleoceanographic investigations.

1.4. Diatoms in Surface Sediments

The distribution of diatoms in surface sediments is related to secondary processes that modify the surface water assemblages, except for autochthonous benthic diatom assemblages. Sedimentation type (Schrader, 1971; von Bodungen, Smetacek, Tilzer, & Zeitzschel, 1985; Smetacek, 1985), lateral transport (Leventer, 1991), and dissolution in the water column and at the water–sediment interface (Kamatani, Ejiri, & Tréguer, 1988; Shemesh, Burckle, & Froelich, 1989) are major processes determining diatom flux to the seafloor. Generally, 1–10% of the diatoms produced in surface waters reach the sediment (Kozlova, 1971; Ragueneau et al., 2000). Although the surface water assemblages, which bear the ecological and climatic signal, are altered during settling to the seafloor and burying, it has been shown that the residual sedimentary assemblages are still indicative of surface conditions in different oceanic regions such as the North Pacific (Sancetta, 1992), the Southern Ocean (Armand et al., 2005; Crosta et al., 2005a; Romero et al., 2005), the Benguela upwelling system (Pokras & Molfino, 1986), the Equatorial Atlantic (Treppke et al., 1996), and the high North Atlantic (Koç-Karpuz & Schrader, 1990; Andersen, Koç, Jennings, & Andrews, 2004a). Diatoms can therefore be used to infer past oceanographic and climatic changes in these regions (Sancetta, 1979; DeFelice & Wise, 1981; Burckle, 1984a, 1984b; Pokras & Molfino, 1987; Pichon et al., 1992; Koç, Jansen, & Haflidason, 1993; Zielinski & Gersonde, 1997).

Autochthonous benthic diatom assemblages result from the ecological preferences of benthic diatoms as described above, and can therefore be used as quantitative paleodepth indicators in coastal areas (Campeau et al., 1999; Jiang, Seidenkrantz, Knudsen, & Eiricksson, 2001).

1.5. Conceptual Progress in Diatom Methods

Diatoms have been known and identified since the beginning of the 18th century, but they have only recently been used to investigate past oceanographic and climatic changes. Three main applications can be described: biostratigraphy for age dating, micropaleontology and geochemistry for paleoceanography.

Fossil diatoms were initially used for biostratigraphic purposes. Biostratigraphy is the science of dating rocks or sediments by using the fossils they contain. Usually, the objective of biostratigraphy is basin-wide correlations when other stratigraphic methods are lacking. The fossil species used must be geographically widespread and have short life spans. Diatom species that achieve these two requirements are key stratigraphic markers. In the 1970s, it was shown that diatom sequences in large regions were similar through time although the sediment composition and texture could be completely different. The different diatom units were tied to paleomagnetic stratigraphy or other biostratigraphy to define Epoch boundaries that one could extrapolate to other records representing the same units, thus ascribing age control at a basin-wide scale. This science is in constant evolution and diatom units are continuously refined due to changing diatom taxonomy, investigations of high-resolution records and better dating techniques. Some key studies are mentioned below, as no further mention of biostratigraphy is made in this chapter.

In the North Pacific, where sediments are mainly barren of $CaCO_3$, diatoms are the prime biostratigraphic tool. Neogene diatom biostratigraphy was developed there in the 1970s (Koizumi, 1977) as a complement to paleomagnetic and tephra chronology. Nineteen diatom zones are currently determined for the Neogene and Pleistocene epochs and are valid for the entire North Pacific (Akiba, 1985; Sancetta & Silvestri, 1984; Akiba & Yanagisawa, 1985). DSDP/ODP cruises (Legs 38, 94, 104, 151, 152, and 162) have shown that the main biogenic component of the Tertiary sediments of the North Atlantic Ocean and the Norwegian-Greenland Sea are the siliceous microfossil group diatoms, and that the area was primarily a silica ocean until the onset of Northern Hemisphere glaciations during the late Miocene. Diatom species show very rapid evolution through the Cenozoic, and this has made it possible to establish a high-resolution biostratigraphy for the area. There is a well-established diatom biostratigraphy for the North Atlantic (Baldauf, 1984, 1987), which has recently been refined (Koç & Flower, 1998; Koç, Hodell, Kleiven, & Labeyrie, 1999; Koç, Labeyrie, Manthé, Flower, & Hodell, 2001). Most of the fossil diatom species of the Norwegian-Greenland Sea are endemic to the area. Therefore, a separate diatom biostratigraphy had to be developed for the Norwegian-Greenland Sea. Based on the DSDP Leg 38 material, Dzinoridze et al. (1978) and Schrader and Fenner (1976) proposed a diatom biostratigraphy for the area. Meanwhile, development of drilling techniques and availability of reliable paleomagnetic stratigraphies enabled the development of a new Neogene (Koç & Scherer, 1996) and late Paleogene (Scherer & Koç, 1996) diatom biostratigraphy for the Norwegian-Greenland Sea based on the ODP Leg 151 material. In the Equatorial Pacific, seven diatom datum levels for the Neogene and Pleistocene epochs were identified and related to the paleomagnetic reversal record (Burckle,1972). Diatom zones are characterized by unique floral assemblages that have proved useful for basin-wide correlations. In the Southern Ocean, McCollum (1975) defined zonal schemes for most of the Tertiary. They were subsequently extended to the Cenozoic (Gersonde, 1990; Fenner, 1991; Gersonde & Barcena, 1998) and recently improved (Zielinski & Gersonde, 2002). Stratigraphic markers from the late MIS 6 at 135 kyr BP, late MIS 7 at 190 kyr BP, and early MIS 8 at 290 kyr BP are again essential to confirm oxygen isotope stratigraphy (Burckle, Clarke, & SHackleton, 1978; Zielinski & Gersonde, 2002).

In the 1980s, paleoceanographers realized that it would be possible to extrapolate the relationships between diatom assemblages in surface sediments and modern parameters to down-core fossil assemblages in order to document past changes in oceanography, in siliceous productivity and ultimately in climate. The starting hypothesis is that a given diatom assemblage is produced and preserved under specific modern conditions. If the same assemblage is found down-core, then oceanographic and climatic conditions may have been the same in the past as they are now. A great number of surface parameters, ecologically important for diatom development, were thus reconstructed: SSTs, SIC, hydrology, productivity events, etc. Initially, investigations were based on down-core variations of given species, or groups of given species, of a known ecology, but it became rapidly apparent that only statistical methods (factor analysis) could provide full understanding of the down-core assemblages and therefore produce better paleoceanographic reconstructions (Burckle, 1984a). The ultimate step was taken in the 1990s with the appearance of transfer functions that provided quantitative estimates of surface properties (Koç-Karpuz & Schrader, 1990; Pichon et al., 1992) and water depth (Campeau et al., 1999), which are essential to constrain or verify paleoclimatic models.

In the 1990s, with the rapid development of isotope geochemistry, it became possible to analyze stable isotopic ratios of light elements in diatoms to track changes in surface water properties. Isotope geochemistry was first applied to foraminifera (Emiliani, 1955, 1966) and then similarly applied to diatoms where carbonated organisms were lacking. Several different and complementary isotopes can be measured in diatoms. Two groups of isotopes detected in diatoms can be differentiated: (1) oxygen (O) and silicon (Si) isotopes that are carried by the diatom frustule, and (2) carbon (C) and nitrogen (N) isotopes that are carried by the organic matrix. This organic matrix is called diatom-intrinsic organic matter (DIOM) and is intimately embedded into the silica lattice where it directs biomineralization (Kröger & Sumper, 1998). Analyzing DIOM rather than bulk organic matter provides a more direct picture of surface water nutrient cycling because the DIOM is protected from remineralization and diagenesis by the silica matrix (Sigman, Altabet, François, McCorkle, & Gaillard, 1999a).

2. IMPROVEMENTS IN METHODOLOGIES AND INTERPRETATIONS

2.1. Micropaleontology

Analysis of microfossil assemblage census counts is one of the principal tools of paleoceanographic studies because distribution of individual organisms and whole ecological systems are affected by the physico-chemical parameters of their habitat. Diatoms are microscopic organisms and should be observed under the microscope at a strong magnification, usually of 1,000. Diatoms must therefore be glued to a permanent medium embedded in between a slide and a cover-slide. Sample preparation is the first laboratory step that will guarantee (or not) a high-quality and reliable study. Additionally, diatomists must follow the same taxonomic references and the same counting rules in an effort of harmonization.

2.1.1. Slide preparation

There are several ways to clean, concentrate, and mount diatom slides, even though all techniques emanate from the original protocol described below (Schrader, 1973). All of them must achieve random settling and random diatom distribution to ensure a good representativity of the sedimentary assemblages.

Generally, the protocol starts by leaching the dry raw sediment with H_2O_2 to remove the organic matter coating the valves, and with HCl to remove carbonates, at a temperature of 65°C. Complete removal has occurred when the bubbling stops. Diatom valves are then concentrated by eliminating the clays through a fractionated settling technique, in which the residue is allowed to sediment for 90 min in a given volume of distilled water. The water, containing not only clays but also some small diatoms, is subsequently removed using a vacuum pump. The settling step is repeated eight times (Schrader & Gersonde, 1978). The final residue is transferred to a 50 ml Nalgene bottle for storage. From this bottle, a given volume is taken after thorough shaking and transferred to another 50 ml Nalgene bottle that serves as a dilution step. A subsample of 0.2 ml is taken from the second bottle after homogenization, and spread on a wet cover-slide hosted in a Petri dish. The water is then evaporated in an oven at 45°C. Permanent mount is achieved by adding a few drops of resin dissolved in xylene or toluene and evaporated on a hot plate.

Variations from this technique include:

- The raw material is freeze-dried instead of dried in the oven. The benefit is that sediment porosity is preserved (Zielinski, 1993).
- Additional boiling of the raw sediment in benzene or tetrasodium diphosphate to stimulate the dispersion of diatom valves (Koç-Karpuz & Schrader, 1990; Pichon, Labracherie, Labeyrie, & Duprat, 1987).
- Transfer of the whole aliquot from the dilution bottle into the Petri dish to ensure better diatom distribution, and use of a paper towel (Koç-Karpuz & Schrader, 1990) or “vaccum” (Scherer, 1995) to suck the water out of the Petri dish after diatom settling.
- Centrifugation of the solution containing the diatom valves instead of the fractionated settling technique to ensure better recovery of small diatoms, transfer of 1–2 drops of the final diluted residue into a prefilled Petri dish, and use of a wool wire to evacuate the water (Pichon et al., 1987; Rathburn, Pichon, Ayress, & DeDeckker, 1997).
- Use of three cover-slides with glue-covered surfaces per sample in one Petri dish (Koç-Karpuz & Schrader, 1990; Zielinski, 1993) or in three different Petri dishes

to avoid artifacts on subsamples during processing (Pichon et al., 1987; Rathburn et al., 1997).

Each protocol presents its own advantages and disadvantages in that the fractionated settling technique may underestimate small diatoms, while the centrifugation technique may destroy very fragile diatoms. Similarly, evaporation of the water contained in the Petri dish yields a better diatom distribution, but takes more time than sucking the water out with a wire, which may displace small diatoms if cover-slides do not have glue-covered surfaces. Finally, using three mounting slides per sample in three different Petri dishes may be statistically more relevant because processing artifacts cannot possibly occur on each subsample.

Recently, a new method based on the different hydrodynamical behavior of diatoms and mineral grains was recently developed (Rings, Lücke, & Schleser, 2004). This method employs split-flow thin fractionation (SPLITT) as a tool for separating diatom frustules from other sedimentary particles. The principle of SPLITT fractionation is the gradual separation of particles in a laminar flow within a tunnel/cell with a field of gravity force applied perpendicular to the flow, the carrier liquid being deionized water. As a result of different sinking velocities, which depend on the density, shape, and size of the particles, particles are separated into two fractions with diatoms escaping the SPLITT by the upper outlet and sedimentary particles flowing through the lower outlet. Length, breadth, and height of the SPLITT channel can be adjusted to obtain the best separation whatever the sediment composition. Advantages of SPLITT fractionation over other techniques are good reproducibility, minimum loss of diatoms, and minimum contamination of diatoms by terrigenous particles and sponge spicules (Rings et al., 2004).

2.1.2. Diatom counts

It is absolutely necessary to follow a few counting rules in order for diatom abundances to be directly compared from site to site and from laboratory to laboratory. A reference convention was developed by Schrader and Gersonde (1978).

Generally, more than half of the valve must be seen to count one specimen (Figure 2). However, some diatom types have particularities, and the reference convention needed to be amended. For example, *Rhizosolenia* type specimens are centric diatoms, and they can reach extreme lengths by increasing their number of girdle bands, but the valve itself is short and circular, and has a spine-like proboscis that it is absolutely necessary to identify in order to count one specimen (Armand & Zielinski, 2001). If only the girdle bands or a part of the proboscis are observed, no specimen is identified (Figure 2). *Thalassiothrix* type specimens are very long and narrow pennate diatoms, and can be broken into hundreds of pieces in the sediment. *Thalassiothrix* relative abundances were estimated from the number of fragments (Pichon et al., 1992), but it was rapidly understood that there is a weak relationship between the number of fragments and the number of valves, since valves can randomly break into few or numerous pieces. Only apices can give an idea of the number of valves, as two apices represent one valve. The number of apices counted in one sample is therefore divided by two to calculate *Thalassiothrix* relative abundance while intermediate fragments are rejected (Armand, 1997) (Figure 2).

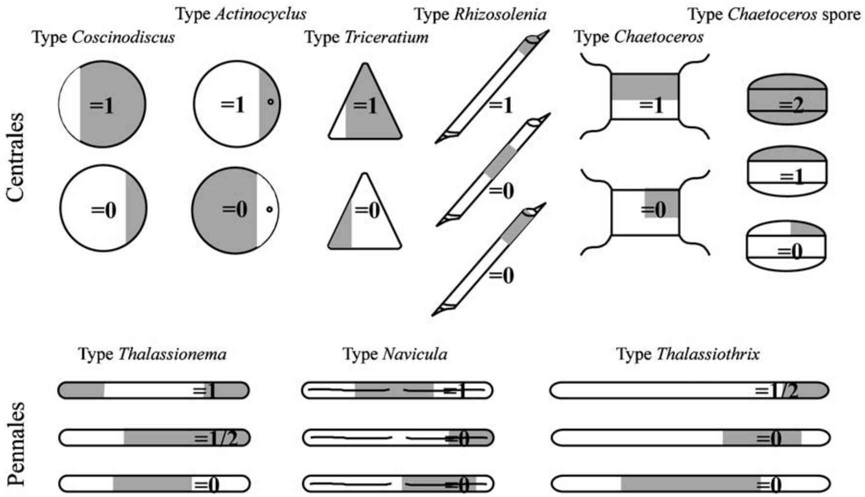


Figure 2 Counting convention for the main diatom groups. The shaded area represents diatom fragments that can be encountered in slides. Redrawn and modified with permission from Schrader and Gersonde (1978) and Armand (1997).

Chaetoceros is another complex genus in which vegetative valves are readily identified but barely preserved in the sediment, particularly in the case of *Hyalochaete* specimens, and resting spores are difficult to identify but are sometimes very abundant in coastal sediments (Leventer, 1991; Crosta, Pichon, & Labracherie, 1997; Hay, Pienitz, & Thompson, 2003). The picture is also often complicated by the presence of numerous pieces of setae. The same rule applies to *Chaetoceros* vegetative cells and resting spores just as for other diatoms, i.e., that more than half of the valve should be present to be counted as one, except that different species are generally lumped together in a *Phaeoceros* group and a *Hyalochaete* group. However, some particularities arise since full resting spore cells have two valves and setae are not counted.

Generally, more than 300–400 specimens should be counted to ensure a good statistical reproducibility. When *Chaetoceros* resting spores are overwhelming (>40–50%), 300–400 specimens other than *Chaetoceros* should be counted to provide an accurate picture of the diatom diversity, and therefore provide better confidence in the paleoceanographic reconstructions (Allen, Pike, Pudsey, & Leventer, 2005).

2.1.3. Diatom assemblages: from presence/absence to statistics

Fossil diatom assemblages can be used to track past environmental changes if (1) modern assemblages are representative of the environmental conditions in which they grow and (2) that diatom ecology has not changed through time.

Relationships with surface parameters. Many papers have shown that diatom assemblages in surface water generally respond to local-to-regional parameters such as nutrient content, water dynamics (currents, hydrological fronts, stratification, etc.), SST, and SIC. In upwelling systems, the main environmental parameter is the intensity of the upwelling that dictates the nutrient input from deep waters and the subsequent nutrient gradient in surface waters. As deep waters are colder than surface waters it also creates a temperature gradient. Diatoms are then distributed in relation to the nutrient and SST gradients. Diatoms having high nutrient requirements thrive closer to the upwelling cell than diatoms having low nutrient requirements. For example, *Chaetoceros* thrives in tropical to polar waters of very high productivity (Hendey, 1937; Pokras & Molfino, 1986; Abrantes, 1988a; Leventer, 1991), while *Fragilariopsis doliolus* thrives in tropical to temperate waters of low to moderate productivity (Simonsen, 1974; Romero, Fischer, Lange, & Wefer, 2000), and *Roperia tessalata* thrives in warm waters of low to moderate productivity (Hasle & Syvertsen, 1997; Semina, 2003).

Most of the time, fossil diatoms preserved in surface sediments have geographical distributions in relation to their ecological preferences. High relative abundances of a given species are found in sediments underlying their maximum production zone in surface waters, where an optimal set of environmental conditions allows the species to develop. Fossil diatoms therefore experience distribution in gradients from high abundances indicating favorable overlying conditions, to low abundances indicating unfavorable conditions. In upwelling systems, favorable conditions are adequate nutrient concentrations and temperatures (Pokras & Molfino, 1986), while in the polar oceans favorable conditions are temperatures and sea-ice cover (DeFelice & Wise, 1981; Koç-Karpuz & Schrader, 1990; Zielinski & Gersonde, 1997). In the Southern Ocean diatoms generally show north–south gradients of increasing or decreasing abundances depending upon their ecological preferences for warmer or colder temperatures, whereas in the Nordic Seas they mainly display east–west gradients ranging from the warm Atlantic current in the east to the sea-ice in the west.

In the Southern Ocean, *F. curta*, the main sea-ice diatom (Armand et al., 2005), reaches its highest relative abundances of ~70% at very cold SSTs between −1°C and 1°C, and heavy sea-ice cover between 8 and 11 months per year (Figure 3). Relative abundances of this species sharply drop to zero at warmer SSTs and lower sea-ice cover. *F. kerguelensis*, the main open ocean diatom (Crosta et al., 2005a), reaches maximum relative abundances of ~80% at SSTs between 1°C and 7°C and low sea-ice cover between 0 and 3 months per year (Figure 3). Relative abundances of *F. kerguelensis* sharply drop to zero at lower SSTs, but drop more gently towards warmer SSTs where it is replaced by species thriving in warmer waters. *F. kerguelensis* also shows an inverse relationship with sea-ice cover that inhibits its production but promotes sea-ice diatom (*F. curta*) production. The *Azpeitia tabularis* group, one of the main warm water diatoms in the Southern Ocean (Romero et al., 2005), reaches highest relative abundances at SSTs between 11°C and 14°C and no sea-ice cover (Figure 3). Relative abundances of this group decrease towards both colder and warmer SSTs.

In most of the cases, maximum abundances of fossil diatoms reflect narrow ranges of environmental conditions (Figure 3). Additionally, overlaps of diatom gradients are common with maximum abundances of species 1 occurring during a decreasing

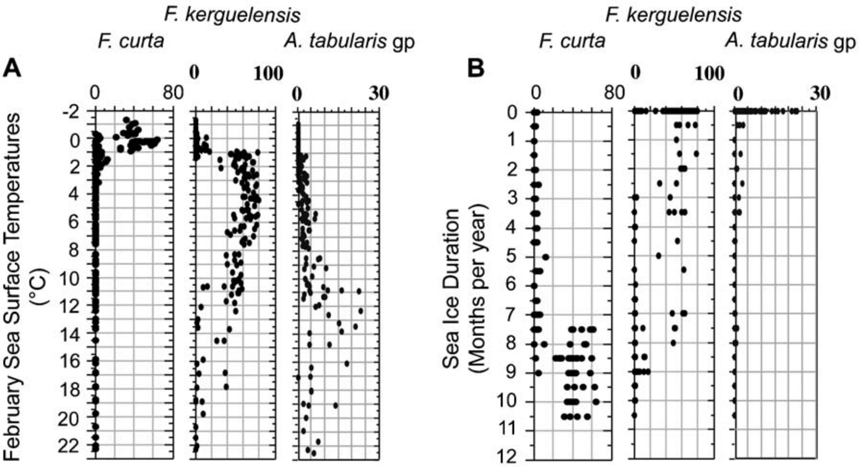


Figure 3 Relative abundances of *Fragilariopsis curta*, *Fragilariopsis kerguelensis* and the *Azpeitia tabularis* group in 228 surface sediment samples from the Southern Ocean versus sea-surface temperatures (A) and sea-ice presence (B). Modified with permission from Armand et al. (2005), Crosta et al. (2005a), and Romero et al. (2005).

trend of species 2 and an increasing trend of species 3. For example, the sharp decrease in *F. kerguelensis* maximum abundances centered at 1°C occurs concomitantly to the appearance of *F. curta*, and the decreasing abundances of *F. kerguelensis* towards warmer waters occur concomitantly to the increasing abundances trend of the *A. tabularis* group (Figure 3). These are some of the specificities that paleoceanographers use to reconstruct past changes. At a given site, down-core changes in the relative abundances of one or several diatom species indicate changes in the environmental conditions. The main challenge is to quantify the type and the magnitude of the changes.

One must keep in mind that preserved fossil assemblages and diatom biogeography is not a direct picture of surface conditions since most of the information is lost during settling to the seafloor. Dissolution, grazing, winnowing, transport, reworking, and bioturbation may deeply alter the surface water assemblages. Sedimentary assemblages therefore represent average surface conditions. The average time covered by the sedimentary assemblage depends on the sedimentation rate, about few centimeters per thousands of years in the open ocean, to a few meters per thousands of years in upwelling systems, coastal areas, and fjords. Some laminated records from exceptional sites allow reconstruction of seasonal signals (Kemp, 1995; Kemp, Baldauf, & Pearce, 1995; Stickley et al., 2005). Still, it is possible to use what we know about regional diatom ecology to reconstruct environmental changes in the past. It can be done by looking at down-core records of a single species, of species ratios or of the total assemblage through statistical methods.

Single species-based reconstructions. Investigation of down-core records of a single species provides information on very specific parameters in restricted areas.

This approach is obviously limited to the range of the species distribution relative to the parameters and requires a very good knowledge of the ecology and distribution of the species. Indeed, diatoms may have different behavior in different environments. Extrapolation of the regional behavior of a given species to another area may lead to spurious interpretation of past changes. Additionally, a resistant species may be concentrated by dissolution, transport, and reworking during settling and burying. One should therefore be careful when using down-core records of a single species to infer paleoceanography and paleoclimate. An example of this type of dichotomic ecology in different environments may be found in the Southern Ocean. Based on extensive investigations of time-series sediment-traps and diatom distribution in surface sediment of the Weddell Sea, Gersonde and Zielinski (2000) showed that relative abundances of the *F. curta* group (*F. curta* and *F. cylindrus*), which were greater than 3% of the total diatom assemblage, indicated the presence of winter sea-ice. They also showed that relative amounts of *F. obliquecostata*, which were greater than 3%, indicated the presence of summer sea-ice. Comparisons of winter and summer sea-ice extents at the last glacial maximum (LGM), estimated by the single species proxies with winter and summer sea-ice extents estimated through a transfer function approach, provide very similar results in the South Atlantic sector, while some discrepancies arise in the Indian sector of the Southern Ocean (Gersonde, Crosta, Abelmann, & Armand, 2005). Reasons behind the inter-basin discrepancy between the two micropaleontological methods are still not fully understood, but it seems that different species ecology in the two sectors and specific transport and dissolution in the Indian sector are the two most likely explanations. Variations in the *F. curta* group were further used down-core to track past changes in sea-ice extent. Application of this proxy to several cores from the Atlantic sector of the Southern Ocean showed rapid sea-ice retreats during deglaciations in phase with SST warming (Bianchi & Gersonde, 2002, 2004).

Species ratios-based reconstructions. Investigation of down-core records of species ratios also provides very specific information in restricted areas, as it does for single species. A very good knowledge of the ecology of the species used in the ratio is absolutely necessary. Ratios can involve different species (Shemesh et al., 1989), different varieties of a single species (Fryxell & Prasad, 1990), different stages of a single species or species group (Leventer et al., 1996), or number of fragments to full cells of a single species (Abrantes, 1988a, 1988b).

Based on the observation of modern diatom distribution and dissolution in laboratory experiments, Shemesh et al. (1989) showed a depletion of *F. kerguelensis* (K) relative to *Thalassiosira lentiginosa* (L) when dissolution increases. The preservation index calculated as K/(K+L) gives information on the relative extent of dissolution. Application of the preservation index to Holocene and LGM samples from the Southern Ocean indicated that Holocene and LGM diatoms from the Atlantic sector are equally preserved while Holocene diatoms from the Indian sector are better preserved than LGM diatoms.

Another preservation index, called the fragmentation index, was identified in the upwelling system off Portugal on the basis of diatom fragmentation (Abrantes, 1988a). Application of this fragmentation index, calculated as the number of diatom fragments to the number of full diatom valves, to cores from the upwelling off Portugal indicated variable temporal and spatial diatom dissolution with greater dissolution during Marine Isotope Stage 3 (MIS 3) than during MIS 2, and greater dissolution at the outer upwelling fringe (Abrantes, 1991).

Investigations of the modern distribution of *Eucampia antarctica* in the phytoplankton have shown this species to form morphologically different summer and winter stages, morphologically different terminal and intercalary valves, and morphologically different warm and cold varieties (Fryxell & Prasad, 1990; Fryxell, 1991). The ratio of summer to winter valves in down-core records potentially gives qualitative information on SSTs. Greater ratio values indicate prominence of the summer stage versus the winter stage and therefore warmer annual temperatures (Fryxell, 1991). Similarly, the ratio of terminal to intercalary valves can be used to track sea-ice extent. A lower ratio indicates greater winter diatom production and therefore less sea-ice. Application of this ratio to a sediment core off the Kerguelen Islands in the Indian sector of the Southern Ocean indicates repetitive sea-ice waning and waxing over the last 800,000 yr, in phase with Milankovitch oscillations of Earth obliquity (Kaczmarska, Barbrick, Ehrman, & Cant, 1993). Another productivity index was built on the concomitant presence of *Chaetoceros* resting spores and *Chaetoceros* vegetative cells in the sediment. Resting spores are formed in the vegetative valves when a strong bloom depletes surface water nutrients (Hargraves & French, 1975; Harrison, Conway, Holmes, & Davis, 1977). Higher values of the spores to vegetative valves ratio indicate higher productivity and subsequent nutrient depletion (Leventer, 1991). The down-core record of this ratio shows repetitive changes during the Holocene with a 200–300 yr cyclicity, suggesting that the siliceous productivity in the Antarctic Peninsula region is primarily controlled by solar activity (Leventer et al., 1996).

More regional paleo-reconstructions are generally based on multispecies investigations that provide a greater spatial coverage and a better characterization of surface water parameters. A set of diatom species covers a wider range of conditions than a single species, with each species covering a small range of conditions (Figure 3). A set of diatom species is also more representative of the phytoplanktonic production and is less prone to dissolution and reworking artefacts. This approach, due to the complexity of dealing with many variables, calls for a statistical analysis of the assemblages.

Statistics-based reconstructions. Statistical treatments are used to reduce the number of variables (species) by grouping species exhibiting similar ecological responses together, and used to detect structure in the relationships between variables. The most common method is the Q-mode factor analysis (QFA). The QFA starts with a principal component analysis (PCA) and is followed by a varimax rotation of the selected principal components (PC). The PCA method involves a mathematical procedure that transforms a number of possibly correlated variables into a smaller number of uncorrelated variables called "principal components." The first PC accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible (Pielou, 1984). In this way, one can find directions in which the data set has the most significant amounts of variation. Species grouping is obtained from the projection of the species squared weights on the space defined by the PC. The QFA is used to study the patterns of relationship among many dependent variables, with the goal of discovering something about the nature of the independent variables that affect them. The inferred independent variables are called "factors." The extraction of factors amounts to a variance maximizing (varimax) rotation of the original variable space defined by the PC. This type of rotation is called variance maximizing because the goal of the rotation is to maximize the variance of the "new" variable (factor), while minimizing the variance around the new variable (Imbrie & Kipp, 1971). The QFA provides two matrices; first, the varimax score matrix that presents the variance accounted for by the factors in each sample and second, the varimax score factor matrix that represents the species weight in each factor. In the varimax factor matrix, the sum of the squares of the factor loadings, defined as the communality of the sample, provides a way of testing the significance of the statistical treatment applied, while the cumulated factor loadings of each factor, called the variance, indicates the significance of each factor in the total data set. Samples belong to the factor in which they reach the highest factor loading. Mapping factor loadings gives information on the geographical extent of the factors. The varimax score factor matrix is most useful to draw preliminary relationships between the factors and environmental conditions based on the ecology of the species included in each factor.

The QFA input data are generally relative abundances of diatom species, but it is sometimes necessary to transform the percent data to reduce the overrepresentation of some species. Class ranking (Pichon et al., 1992) or logarithmic transformation of the relative abundances (Zielinski, Gersonde, Sieger, & Fütterer, 1998) may be used to this effect.

In order to develop a calibration set for paleo-reconstructions, the first step is to apply the QFA to modern samples to extract and map factors and to draw a relationship between the factors and modern environmental conditions. Generally, not all of the species present in the surface sediments are used. Rare diatom species (less than 2% of the total assemblage), reworked species, widely distributed species and benthic species are eliminated because they do not highlight specific surface conditions. Input or not of a diatom species obviously depends on the parameters to be reconstructed. The second step is to apply the same statistical treatment to the same species counted down-core. The same factors are extracted for each fossil assemblage. From the down-core evolution of factor dominance it is possible to infer past oceanographic changes at the core location.

Such a statistical approach has been widely used in the 1980s. Sancetta (1979) applied a QFA treatment to diatom assemblages in 62 core-top samples from the North Pacific that resolved Subtropical, Transitional, Subarctic, Production, and Okhotsk factors with clear relationships to regional water types and currents. The five factors accounted for 96% of the total variance. The QFA treatment of diatom assemblages in a series of cores indicated a strong cooling of surface and deep waters and higher productivity in the northwestern Pacific during the last glacial. A QFA analysis of diatom assemblages in 59 core-tops from the Eastern Equatorial Atlantic derived Tropical — Moderate Productivity, High Productive, Runoff, Subtropical

— Low Productivity and Antarctic Displaced factors (Pokras & Molfino, 1986). Each factor presents a different dominant diatom species or species association. The five factors accounted for 95% of the original variance. When applied to a set of cores, the QFA approach indicated strong variations of the factors in phase with climate changes. Higher diatom productivity in the Equatorial Atlantic during glacial MIS 2, 4, and 6, and low diatom productivity during the warm substage 5.5 were observed (Pokras & Molfino, 1987). Based on very low scores of the Antarctic Displaced factor, influx of Antarctic Bottom Water was supposed insignificant throughout the last 160,000 yr. Factor analysis of diatoms in 55 core-tops from the Southern Ocean produced Sea-Ice, Polar Front Zone, and Antarctic Zone factors, the latter one being encompassed by the two first factors (Burckle, 1984a). The three factors accounted for 97% of the total variance. A QFA of the same 27 diatom species in 51 fossil samples showed the distribution of these factors during the LGM. For each factor, high factor loadings were generally located more to the north than their modern distribution, indicating a northward migration of the Polar Front Zone, of the winter sea-ice and a strengthening of the Weddell Gyre in relation with colder temperatures and stronger winds.

2.1.4. Transfer functions

Presence/absence of a diatom species, relative abundance variations of one or several species, and QFA on many species provide qualitative interpretation of past environmental changes. Transfer functions go a step further and produce quantitative estimates of surface physico-chemical parameters, such as SSTs in degree Celsius, thanks to the development of advanced computational methods. Such quantitative estimates are essential because they are independent of geochemical proxies and are most useful to constrain or validate paleoclimatic models. They provide a range of values in which model results may fall if the physics are correctly computed (Kucera, Rosell-Melé, Schneider, Walbroeck, & Weilnet, 2005).

A transfer function must be understood as any kind of mathematical approach that analyses census counts of fossil assemblages to produce absolute values of surface properties by comparing fossil samples to a subset of modern samples having definite modern conditions. Transfer functions can work on reduced species data sets but generally between 20 and 40 diatom species are used. Reduced species data sets can perform better than raw data sets because the high variability of the diatom assemblages is smoothed (Racca, Gregory-Eaves, Pientiz, & Prairie, 2004). Similarly, although it is possible to work on limited surface sample data sets, it may be best to work on extended data sets that cover broader modern conditions, hence reducing the possibility of nonanalog conditions. There are several types of transfer functions, each one based on different mathematics. The most common ones are the Imbrie and Kipp Method (IKM; Imbrie & Kipp, 1971), the Modern Analog Technique (MAT; Hutson, 1980), the Weighted Averaging Partial Least Square (WA-PLS; ter Braak & Juggins, 1993), Maximum Likelihood (ML; Birks & Koç, 2002), and the Artificial Neural Network method (ANN; Malmgren & Nordlund, 1997; Malmgren, Kucera, Nyberg, & Waelbroeck, 2001). The General Additive Model (GAM; Armand, 1997) and the Revised Analog Method (RAM;

Waelbroeck et al., 1998) are variations of the IKM and MAT approaches, respectively.

All transfer functions operate within the same framework. Whatever the algorithms and the techniques used, they all start with three databases. First, the modern species database that displays the chosen diatom species present in core-top sediments (Figure 4). This data set is the same as the one used in the QFA mentioned above. Second, the modern parameter database that gives quantitative values of surface properties extracted from *in situ* measurements, generally compiled in numerical atlases. Values are extracted at the vertical of the core-top samples, as it is impossible to cope with lateral advection of sinking particles in extended databases. Third, the fossil species database that includes diatom census counts of the same species in down-core samples. Whatever the algorithms and the techniques used, most transfer functions work in three steps. First, the calibration step compares the modern species database to the modern parameter database to determine species–environment relationships between the two sets (Figure 4). Second, the comparison step correlates the fossil database to the modern database to detect similarities between the two sets. Third, the estimation step produces the quantitative estimate based on the two first steps.

Each technique is dependent upon, but differently affected by, the quality of the three databases and therefore upon diatom taxonomy, core-top coverage, and the extraction of the modern parameters. Databases are thus validated through an auto-run of the modern data sets to check whether modern surface properties are accurately estimated. The modern database serves therefore as both the reference database and the fossil database. Good databases and appropriate transfer functions will provide paleoenviromental estimates close to the modern environmental values

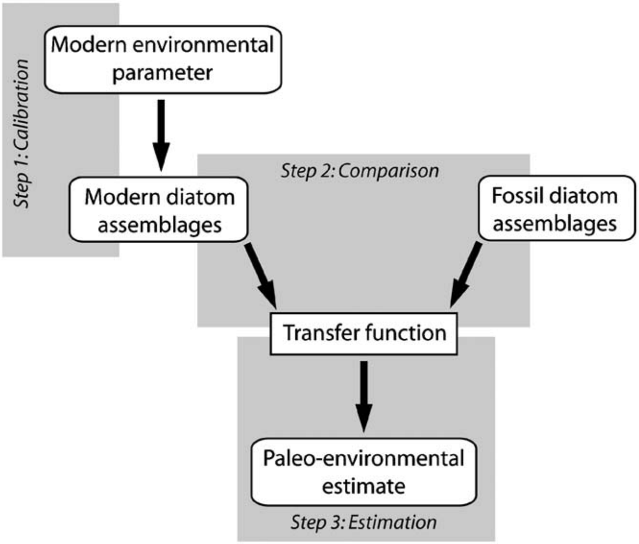


Figure 4 Schematic protocol of a transfer function highlighting the databases and the three-step mathematical technique.

associated with each sample. Linear regression between observed and estimated values must yield a correlation coefficient and a slope close to 1, low residuals and low standard errors on the estimates. When it is validated, the whole package, including the databases and the mathematical approach, can be applied to fossil samples.

The IKM is based on a QFA of the core-top diatom assemblages (program CABFAC) and a regression between the calculated factors and the modern parameters (program REGRESS) that builds the paleoecological equation (Figure 4, step 1). The fossil diatom assemblages are also reduced through a QFA (Figure 4, step 2). Factor loadings of each fossil assemblage are then introduced into the paleoecological equation (program THREAD) to produce the quantitative paleoenvironmental estimate (Figure 4, step 3). The IKM is possibly the best technique to apply on restricted modern databases because it calculates a mathematical function between the core-tops samples and the parameters, thus coping with the lack of samples. The program CABFAC provides information on the biogeography of the modern factors and on the representativity of the chosen species in the assemblages. The communality is a good tool to discard core-tops that are possibly affected by dissolution, reworking, or are just not represented by the chosen factors. The IKM allows extrapolation, i.e., paleoenvironmental estimates outside the range of values covered by the modern parameter database. Conversely, the paleo-equation also has important flaws in that (1) it only provides a mean standard error on the equation, (2) it smoothes the estimates, and (3) it is affected by addition of any modern sample that will subsequently change the estimates. Moreover, this technique is strongly influenced by species with high relative percentages, at least in Southern Ocean sediments. This dependency upon overrepresented species should be alleviated through normalization of the diatom relative abundances using a system of class ranking (Pichon et al., 1987) or logarithmic transformation (Zielinski et al., 1998). Different systems of normalization induce different estimates.

The MAT is a simple comparison between fossil assemblages and modern ones. There is no calibration step besides plots of species relative abundances in core-top samples versus associated parameters. For each fossil sample, a dissimilarity coefficient, which measures the difference between the fossil assemblage and the modern assemblages, is calculated using the square chord distance (Hutson, 1980). The MAT then chooses the x less dissimilar analogs to calculate the paleoenvironmental estimate. This calculation can be a simple average of the x quantitative values associated with the chosen analogs (Prell, 1985), or an average of the x values weighted by the geographical distance of the analogs to the fossil sample (Pflaumann, Duprat, Pujol, & Labeyrie, 1996), or weighted by the dissimilarity coefficients (Guiot, 1990). This approach generally works with relative percentages and does not require normalization of the relative abundances, because rare species with low abundances are as equally important as dominant species. As the estimate is a simple average of the core-top parameter values, the MAT provides a root mean square error of prediction (RMSEP) for each fossil sample, and therefore a point-by-point control of the paleoenvironmental estimate. Any new core-top sample can be added to the modern database and can contribute to the result of any fossil samples without changing the whole set of estimates. The MAT provides the location of the chosen analogs that may give further environmental information than the quantitative estimate. However, the MAT has several flaws. It requires an extended core-top database to provide reliable analogs to any fossil sample. It is very sensitive to the number of chosen analogs and to the maximum value of dissimilarity above which the analog is rejected and not used in the calculation of the paleoenvironmental estimate. Estimates are restricted to the range of values covered by the modern databases.

WA-PLS can be regarded as the unimodal-based equivalent of multiple linear regressions (ter Braak & Juggins, 1993). This means that a species has an optimal abundance along the environmental gradient being investigated. As with the IKM method, WA-PLS uses several components in the final transfer function. These components are however selected to maximize the covariance between the environmental variables to be reconstructed and hence the better predictive power of the method, whereas in the IKM method the components are chosen irrespective of their predictive value to capture the maximum variance within the biological data.

The ANN works using a back propagation (BP) neural network, which relies on the hypothesis that there is a relationship between the distribution of modern assemblages and the physical and chemical properties of the environment. The ANN is based on an algorithm that has the ability of autonomous "learning" of a relationship between two groups of numbers (Malmgren & Nordlund, 1997), by exchanging information between the interconnected processing units composing the network. The learning persists as long as the prediction error for each sample in the calibration data set decreases and provides a calibration equation calculated on the modern databases. The ANN is best when relationships between core-top assemblages and surface properties are nonlinear. It is not dependent upon the size of the modern database and it allows extrapolation similarly to the IKM. Nevertheless, this technique has several flaws. The ANN calibration is more or less a black box and it is extremely time-consuming because of the learning period. Different architectures of the network yield different estimates.

2.2. Isotope Geochemistry

Isotope analyses were first developed for bulk sediment (N isotopes) or for organisms other than diatoms (C and N isotopes). They were eventually applied to diatoms to cope with important diagenetic problems or wherever carbonate organisms were not present. Up until now, four isotope ratios are routinely measured in the diatom organic-intrinsic matter (C and N) and in the diatom frustule (O and Si). Specific protocols that are developed in the following paragraphs were built to extract and purify diatoms from the bulk sediment.

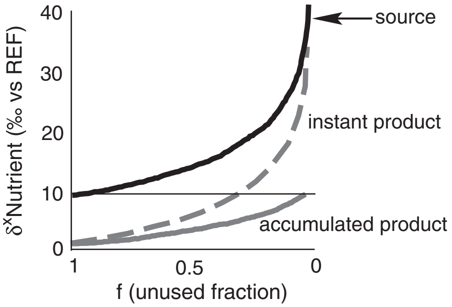
2.2.1. Rationale behind the isotopes

Diatoms preferentially assimilate light isotopes (^{12}C, ^{14}N, ^{16}O and ^{28}Si) to build the organic matter and biomineralize the frustules, thus leaving the nutrient pool in surface waters enriched in heavy isotopes (^{13}C, ^{15}N, ^{18}O and ^{30}Si). As the initial nutrient pools are consumed during biomass production, their nutrient light to heavy isotope ratios progressively increase. This progressive increase is transferred to the biogenic material subsequently produced using the enriched pool, thus leading to a parallel isotope enrichment of the organic material (Figure 5). Stable isotope ratios of the particulate organic matter and of the buried organic matter reflect the proportion of nutrients assimilated during phytoplankton development as a measure of the balance between supply to the surface waters and biological uptake. Therefore, they do not represent an absolute value of the assimilation but rather a relative uptake of the nutrient.

The isotopic signal, noted δ, provides a way to visualize the isotopic enrichment of the source and of the product. Additionally, δ is calibrated versus reference values used worldwide that allow for intercomparisons. Standard notation for δ is depicted in Equation (1) where E is the element, H is the heavy isotope and L is the light isotope (Figure 5). δ may therefore be understood as a deviation from the reference isotopic ratio values.

The isotopic enrichment between the organic product and the dissolved nutrients is calculated as fractionation factor α that measures the reactivity of an organism to the various isotopes of an element. The fractionation factor is determined at equilibrium and is dependent upon physico-chemical and environmental factors. Because it is expressed as the ratio of heavy to light isotope ratios in the source and the product, α is very close to 1. Isotope geochemists therefore prefer to use the fractionation, ε_p, which represents the deviation from 1. The higher ε_p is, the less heavy isotopes are assimilated, which results in more depleted δ values in the biogenic material (Figure 5 and equation (2)). In Rayleigh's model, a constant ε_p yields at any moment an instant product δ (dotted gray line) depleted by ε_p regarding the source δ (black line) (Figure 5 and equation (3)). The integrated

$$\delta^xE = \{[(^HE/^LE)\mathrm{sample} / (^HE/^LE)\mathrm{reference}] - 1\} * 1000 \qquad (1)$$



$$\delta^x\mathrm{Nut} = \delta^x\mathrm{Nut}_{\mathrm{initial}} - \varepsilon * \ln(f) \qquad (2)$$

$$\delta^x\mathrm{IP}_t = \delta^x\mathrm{Nut}_t - \varepsilon \qquad (3)$$

$$\delta^x\mathrm{AP}_t = \delta^x\mathrm{Nut}_{\mathrm{initial}} + [f/(1-f) * \varepsilon * \ln(f)] \qquad (4)$$

Figure 5 Simulation of nutrient fractionation during biogenic material formation by diatoms. Curves depict changes in the delta of the source (black line), of the instant biogenic product (dotted gray line) and of the accumulating biogenic product (gray line). Nut = nutrient; ε = fractionation; f = unused nutrient fraction; E = element; H = heavy isotope; and L = light isotope.

product δ has the same value as the source initial δ value when all nutrients are used (Figure 5 and equation (4)).

2.2.2. Carbon isotope ratios in diatoms

On wide oceanic scales, the $\delta^{13}C_{org}$ is anticorrelated with the concentration of molecular dissolved CO_2 ($CO_{2(aq)}$) in surface waters (Rau, Froelich, Takahashi, & Marais, 1989, 1991a). The $CO_{2(aq)}$ is dependent upon physical processes (SST and salinity, diffusivity, wind intensity) and biological processes (carbon uptake). It was believed that passive diffusion into phytoplankton cells was the primary carbon acquisition pathway (Laws, Popp, Bidigare, Kennicutt, & Macko, 1995), and therefore $\delta^{13}C_{org}$ down-core records were tentatively used to reconstruct past CO_2 concentrations in surface waters (Jasper & Hayes, 1990; Bentaleb & Fontugne, 1998). However, the anticorrelation between $\delta^{13}C_{org}$ and $CO_{2(aq)}$ is not consistently observed regionally within a given ocean system when other factors may become dominant, such as growth rate, community structure (Popp et al., 1999), cell size/shape fraction (Pancost, Freeman, Wakeham, & Robertson, 1997; Popp et al., 1998; Burkhardt, Riebesell, & Zondervan, 1999; Trull & Armand, 2001), and nondiffusive carbon uptake through carbon concentration mechanisms (Rau, 2001; Tortell, Rau, & Morel, 2000; Tortell & Morel, 2002; Cassar, Laws, Bidigare, & Popp, 2004; Woodworth et al., 2004). These processes, by strongly affecting the carbon isotopic fractionation (ε_p), weaken the relationship between $\delta^{13}C_{org}$ and $CO_{2(aq)}$, and may account for the discrepancy between marine $\delta^{13}C_{org}$-based pCO_2 reconstructed from low-latitude records and Vostok CO_2 (Kienast, Calvert, Pelejero, & Grimalt, 2001).

The cleaning procedure to isolate DIOM follows the method described by Singer and Shemesh (1995), which involves a decarbonation, a stepwise physical washing and sieving at 32 μm in order to separate the diatom fraction from the bulk sediment, a heavy liquid step to remove the heavy minerals, and an oxidation of the labile organic matter of the diatom fraction <32 μm to remove the labile organic matter coating the diatom valves. The advantages of using the fraction <32 μm are that (1) it generally accounts for the largest amount of the whole diatom assemblage, (2) the same species generally dominate down-core records, and (3) no radiolarians or sponge spicules are present.

Analyses of DIOM-$\delta^{13}C_{org}$ are therefore performed on a restricted diatom size fraction that may limit the influence of community structure and cell size/shape changes, thus providing a more direct link to $CO_{2(aq)}$ and phytoplankton carbon uptake as a mirror of paleoproductivity changes (Shemesh, Macko, Charles, & Rau, 1993; Singer & Shemesh, 1995; Rosenthal, Dahan, & Shemesh, 2000; Crosta & Shemesh, 2002). Analyses of DIOM-$\delta^{13}C_{org}$ are also conducted on a specific organic matter, mainly composed of proteins (Kröger & Sumper, 1998; Kröger, Bergsdorf, & Sumper, 2002), which directs biomineralization of the frustule (Kröger, Deutzmann, & Sumper, 1999). This organic matter is protected from alteration and diagenesis by the silica matrix (Sigman et al., 1999a; Crosta, Shemesh, Salvignac, Gildor, & Yam, 2002), again providing a more faithful picture of processes occurring in surface waters. It is, however, important to keep in mind that analysis of the DIOM only limits the issues mentioned above, and that many unknowns still exist.

Up until now, investigations of DIOM-$\delta^{13}C_{org}$ were exclusively conducted in the Southern Ocean to document past changes in productivity and nutrient cycling in relation to oceanographic and climate changes. Comparison of several downcore records of DIOM-$\delta^{13}C_{org}$ with other productivity proxies (Mortlock et al., 1991; Kumar, Gwiazda, Anderson, & Froelich, 1993, 1995; Anderson et al., 1998; Bareille et al., 1998; Frank et al., 2000; Dézileau, Reyss, & Lemoine, 2003) have shown a glacial drop in productivity south of the Antarctic Polar Front, a glacial increase in productivity in the Subantarctic Zone, and no glacial changes in productivity in the Subtropical Zone (Shemesh et al., 1993; Singer & Shemesh, 1995; Rosenthal et al., 2000; Crosta & Shemesh, 2002; Crosta et al., 2005b).

2.2.3. Nitrogen isotope ratios in diatoms

In many oceanic regions, the $\delta^{15}N_{org}$ of sinking bulk organic matter is correlated to the relative uptake of nitrate in surface waters (Rau, Sullivan, & Gordon, 1991b; Altabet & François, 1994; Sigman, Altabet, McCorkle, François, & Fisher, 1999b). The higher the consumption, the heavier the $\delta^{15}N_{org}$ becomes. More enriched nitrogen isotopes in glacial sediments of the Antarctic Indian Ocean were therefore taken to indicate greater nutrient use during cold periods (François, Altabet, & Burckle, 1992; François et al., 1997), although it was long known that several other factors may influence the sedimentary $\delta^{15}N_{org}$ records. Indeed, bacterial remineralization during sinking and burial preferentially removes ^{14}N, leaving the fossilized organic matter enriched in ^{15}N relative to the organic matter produced in surface waters (Altabet & François, 1994). Early diagenesis similarly leads to the preservation of ^{15}N-enriched organic matter. Such alteration of the surface water signal may be different from place to place and, more importantly, may not be constant through time in a given place. Enrichment can be up to 2–5‰ (Altabet & François, 1994) and is mainly dependent upon the flux and speed of sinking organic matter (Lourey, Trull, & Sigman, 2003), and on the redox conditions at the water–sediment interface (Ganeshram, Pedersen, Calvert, McNeill, & Fontugne, 2000). Analysis of DIOM-$\delta^{15}N_{org}$ allows us to deal with the impact of remineralization and diagenesis because the DIOM is protected from alteration by the frustule (Sigman et al., 1999a; Crosta & Shemesh, 2002). It also reduces the potential impact of community changes, diatom size fraction (Karsh, Trull, Lourey, & Sigman, 2003), and contamination by continental organic matter (Huon, Grousset, Burdloff, Bardoux, & Mariotti, 2002). We are still far from fully understanding bulk $\delta^{15}N_{org}$ and DIOM-$\delta^{15}N_{org}$ signals in the modern ocean because of species-dependent isotopic fractionation factors (Sigman & Casciotti, 2001) and of different nutrient sources (Lourey et al., 2003). Uncertainties are even higher for the past oceans due to the preservation state of the organic matter and the diatoms.

Although bulk $\delta^{15}N_{org}$ measurements have been conducted in many places (François et al., 1997; Kienast, Calvert, & Pedersen, 2002; Higginson, Maxwell, & Altabet, 2003; Galbraith, Kienast, Pedersen, & Calvert, 2004, and references cited therein; Higginson & Altabet, 2004), DIOM-$\delta^{15}N_{org}$ investigations are restricted to the Southern Ocean (Shemesh et al., 1993, 2002; Sigman et al., 1999a; Sigman

& Boyle, 2000; Hodell et al., 2001; Crosta & Shemesh, 2002; Robinson, Brunelle, & Sigman, 2004, 2005; Crosta et al., 2005b). The cleaning procedure follows the one described above for the DIOM-$\delta^{13}C_{org}$ analysis. Combustion-based measurement of DIOM-$\delta^{15}N_{org}$ is generally performed simultaneously to the DIOM-$\delta^{13}C_{org}$ analysis (Crosta & Shemesh, 2002), although DIOM-$\delta^{15}N_{org}$ can be measured alone on the IRMS to gain sensitivity and reproducibility. Another technique involving conversion of DIOM nitrogen to nitrate and denitrification of the resulting nitrate into N_2, which is subsequently introduced into the IRMS, was recently developed (Sigman et al., 2001). This method reduces the amount of N_{org} necessary to attain the detection level and alleviates the potential air contamination introduced during the combustion-based protocol (Robinson et al., 2004). The persulfate-denitrifier method leads to different results in the Antarctic Zone, but to similar results in the Subantarctic Zone relative to the combustion-based method (Robinson et al., 2004, 2005; Crosta et al., 2005b). Why these discrepancies exist between the two methods is still under debate.

DIOM-$\delta^{15}N_{org}$ investigations, coupled with other paleoproductivity proxies, indicate increased relative uptake of nitrate in the Antarctic and Subantarctic Zones and no changes in uptake in the Subtropical Zone during the last glacial period. The reason for increased relative uptake of nitrate is regionally different. South of the Antarctic Polar Front, heavier DIOM-$\delta^{15}N_{org}$ values result from reduced nutrient supply in the surface waters, certainly in relation to stratification of surface waters by greater glacial sea-ice melting (François et al., 1997). In the Subantarctic Zone, heavier DIOM-$\delta^{15}N_{org}$ values result from an increase in glacial productivity and iron fertilization promoting the N/Si uptake ratio by diatoms (Crosta et al., 2005b; Robinson et al., 2005).

2.2.4. Silicon isotope ratios in diatoms

Laboratory-culture experiments and *in situ* investigations have shown that the $\delta^{30}Si$ of diatoms is correlated to the relative uptake of silicic acid ($Si(OH)_4$) by diatoms in surface water (De la Rocha, Brzezinski, DeNiro, & Shemesh, 1998; Varela, Pride, & Brzezinski, 2004). From the few studies made, it seems that silicon fractionation is independent of temperature and diatom species, although silicon ε_p measured in low-temperature waters of the Southern Ocean was twice as high (Varela et al., 2004) compared to temperate culture batches (De la Rocha, Brzezinski, & DeNiro, 1997). Additional investigations are required to fill in several gaps in our knowledge. Also, it seems that $Si(OH)_4$ is the only silicon source and that frustule dissolution does not modify the sedimentary isotopic silicon composition of diatoms (De la Rocha et al., 1998), thus facilitating paleoceanographic interpretations.

The analytical protocol to measure $\delta^{30}Si$ in diatoms involves the recovery and purification of the silicon as SiO_2 and the fluorination of the purified silica to form SiF_4 gas, which is subsequently injected into the IRMS (De la Rocha et al., 1997). However, strong leaching with HF and laser heating render this technique tedious and dangerous. New techniques to measure silicon isotopes by MC-ICP-MS using dry plasma conditions are under development (De la Rocha, 2002; Cardinal et al., 2003). This new method provides better accuracy than the IRMS technique (less than 0.1‰), which is appreciable when silicon ε_p is 1‰.

Most of δ^{30}Si studies are from the Southern Ocean and more particularly from the Antarctic Zone (De la Rocha et al., 1998; Brzezinski et al., 2002; Beucher, Brzezinski, Crosta, & Tréguer, 2006). In the Antarctic and Subantarctic Zones, δ^{30}Si signals are anticorrelated to DIOM-$\delta^{15}N_{org}$ signals, indicating less silicon uptake and more nitrate uptake during the last glacial period relative to modern times. This shows that surface water stratification is not the only process affecting nutrient cycling and biological uptake. Iron fertilization by dust input or vertical supply is necessary to decouple $Si(OH)_4$ and NO_3^- consumption by diatoms (Hutchins & Bruland, 1998; Takeda, 1998; Crosta et al., 2002). In the Subtropical Zone, δ^{30}Si signals are correlated to DIOM-$\delta^{15}N_{org}$ signals, both indicating almost no change in $Si(OH)_4$ and NO_3^- consumption by diatoms over the last 50,000 yr.

2.2.5. Oxygen isotope ratios in diatoms

The δ^{18}O of diatoms is dependent upon the SST and the isotopic composition of the water in which diatoms formed their frustule (Juillet-Leclerc & Labeyrie, 1987). It seems that the isotopic signal is free of species effect, although more laboratory-culture experiments are necessary to confirm preliminary results. The isotopic composition of the water is tied to salinity (Craig & Gordon, 1965). Equations linking diatom δ^{18}O and SST have been developed. These paleotemperature equations show slopes different than the ones developed for carbonate δ^{18}O, thus allowing the reconstruction of both SST and isotopic composition of the water when foraminifera and diatoms grow in the same water mass (Moschen, Lücke, & Schleser, 2005).

Measurement of δ^{18}O is difficult because of the exchangeable nature of a fraction of oxygen atoms included in the silica matrix. Approximately 10–20% of oxygen is labile, which explains the lack of reproducibility during early investigations (Labeyrie & Juillet, 1982). The fraction of nonexchangeable oxygen is stable over thousands of years and retains the surface water isotopic composition after burial (Shemesh, Charles, & Fairbanks, 1992). The goal of the protocol is to exchange the labile oxygen fraction with oxygen of known isotopic composition under controlled conditions of temperature and water isotopic ratio (Labeyrie & Juillet, 1982). For example, Shemesh, Burckle, and Hays (1995) let pure diatoms react with water vapor at 40‰ during 6 h at 200°C. Pure diatom samples are obtained using a method similar to that used for DIOM-$\delta^{13}C_{org}$, except for a stronger leaching and additional settling and heavy liquid steps in order to completely remove the organic matter, clays, and heavy minerals that alter the isotopic composition of diatom silica (Juillet-Leclerc, 1984; Shemesh et al., 1995). After the exchange, diatoms are recrystallized. The extraction of the oxygen and its conversion to CO_2 is carried out by fluorination. The CO_2 is then analyzed for its oxygen isotopic composition in the IRMS with reproducibility better than 0.2‰. A new technique was recently developed for the determination of oxygen isotope composition in biogenic silica. The inductive high-temperature carbon reduction method (iHTR) is based on the reduction of silica by carbon, using temperatures as high as 1,830°C, to produce carbon monoxide for isotope analysis. Details of this method are presented in Lücke, Moschen, and Schleser (2005). The amount of material necessary is 1.5 mg of biogenic silica, and the reproducibility for natural samples is better than 0.15‰.

Most studies of diatom δ^{18}O have been conducted in the Atlantic sector of the Southern Ocean where they indicate melt-water input during the LGM (Shemesh, Burckle, & Hays, 1994) and the last deglaciation (Shemesh et al., 2002). Diatom δ^{18}O, although difficult to analyze, is a particularly suitable tool to document melt-water events in the Southern Ocean, for example whether MWP 1A originates from Antarctica (Weaver, Saenko, Clarck, & Mitrovica, 2003), since foraminifera are often not present in the sediments during these events.

3. CASE STUDIES

3.1. SST in the North Atlantic

In the North Atlantic and the North Pacific Oceans, diatom-based SST estimates have been generally provided via IKM transfer functions (Sancetta, 1979; Sancetta, Heusser, Labeyrie, Naidu, & Robinson, 1985; Koç et al., 1993; Koç, Jansen, Hald, & Labeyrie, 1996; Andersen, Koç, & Moros, 2004a, 2004b; Jiang, Eiricksson, Schulz, Knudsen, & Seidenkrantz, 2005). Even though the QFA is certainly a good method to cope with the huge range of environmental conditions encountered at high northern latitudes, both WA-PLS and ML are being used more and more often (Birks & Koç, 2002). Transfer functions in the high-latitude North Atlantic have been applied primarily to the deglaciation (Koç-Karpuz & Jansen, 1992) and the Holocene (Koç et al., 1993; Andersen et al., 2004a, 2004b; Jiang et al., 2005). Due to sea-ice cover during the glacial periods it has been almost impossible to obtain long and continuous diatom records from the high-latitude North Atlantic.

As a result of societal pressure in the context of global warming, the focus today is on understanding the frequency and origin of Holocene climate variability in the region of the North Atlantic. This ocean is a key region in modulating the global climate through the thermohaline circulation. More locally, complicated atmospheric and oceanic circulation patterns regulate the amount of heat transported to northern North America and northern Europe. Intensive quantitative reconstructions of climate parameters in this region will help us to understand how atmospheric and oceanic circulation patterns have evolved and interacted during the Holocene, and can then be used to forecast their behavior in the future.

In the example below, an IKM transfer function was applied to diatom fossil assemblages of core MD95-2011 from the Voring Plateau in the Norwegian Sea (66°58.18′N — 07°38.36′E — 1,048 m) (Birks & Koç, 2002; Andersen et al., 2004a). The modern database was composed of 139 core-top samples. The modern species database was composed of 52 species. The QFA calculated eight factors defined by specific diatom assemblages. The eight factors, accounting for 95% of the total variance, are described in detail in Andersen et al. (2004a). The down-core diatom relative abundances were transformed into the same eight factors, which were subsequently introduced into the equation to calculate paleotemperatures. The IKM technique produced in this example a coefficient of determination (R^2)

of 0.9 and a RMSEP of 1.25°C. The chronology of the core was based on 10 AMS dates calibrated to calendar ages using CALIB 4.3 software (Stuiver et al., 1998) after removing the reservoir age, and one tephra layer.

The diatom-based SSTs indicate a division of the Holocene into three periods: first, the Holocene Climate Optimum (HCO) between 9,500 yr B.P. and 6,500 yr B.P. with SSTs around 15°C, i.e., 4°C warmer than the modern SSTs at the core location (Figure 6); second, the Holocene Transition Period (HTP) between 6,500 yr B.P. and 3,000 yr B.P. displaying a SST decrease towards modern values; and third, the Cool Late Holocene Period (CLPH) between 3,000 yr B.P. and 0 yr B.P. with temperature around the modern SST value of 10–11°C. The timing of the CLPH onset at 3,000 yr B.P. seems in phase with the initiation of the global Neoglacial cool period, similarly detected at high Southern latitudes (Leventer, Dunbar, & DeMaster, 1993; Brachfeld, Banerjee, Guyodo, & Acton, 2002; Shevenell & Kennett, 2002).

The reconstructed cooling trend is in agreement with other reconstructions from the same region and from other regions of the North Atlantic (Bauch et al., 2001; Jennings, Knudsen, Hald, Hansen, & Andrews, 2002; Andrews & Giraudeau, 2003). It is also in step with the decreasing Northern Hemisphere summer insolation since the last 10,000 yr, indicating a strong orbital-driven impact on Holocene climate evolution. There are, however, regional discrepancies in the timing and duration of the HCO in particular, indicating complex atmospheric and oceanic responses to the insolation forcing. Specifically, it is believed that an intense cold East Greenland Current associated with greater sea-ice presence led to delayed HCO warming in the western North Atlantic relative to the eastern North Atlantic (Andersen et al., 2004b). A large-scale North Atlantic Oscillation signature influencing wind strength and direction could also explain the reconstructed zonal SST differences.

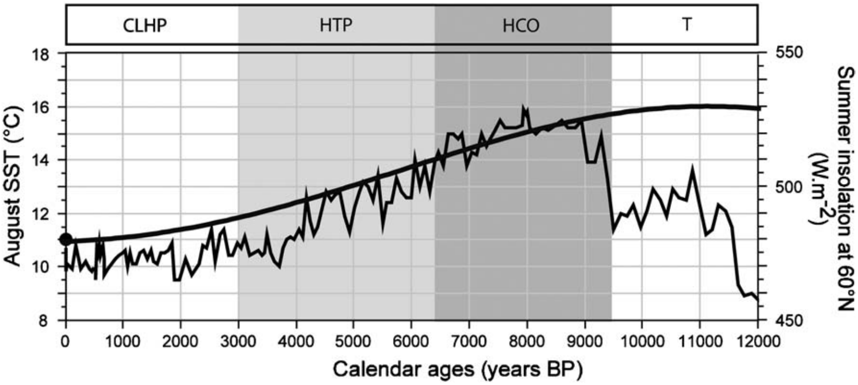


Figure 6 Sea-surface temperatures in core MD95-2011 as estimated by a diatom-based IKM transfer function (modified from Andersen et al., 2004a, 2004b). Modern August SST value is ~11°C (black point), which matches well with the core-top estimate of 10.1°C. Stratigraphy of the core is based on 10 AMS-14C dates and one tephra layer. T: Transition; HCO: Holocene Climatic Optimum; HTP: Holocene Transition Period; CLHP: Cool Late Holocene Period.

3.2. Sea-ice in the Southern Ocean

In the Southern Ocean, diatom-based SST estimates are generally given through IKM and MAT approaches, depending on the modern data set available (Pichon et al., 1992; Zielinski et al., 1998; Crosta, Sturm, Armand, & Pichon, 2004). Estimation of sea-ice winter and summer extents are provided by the *F. curta* and *Fragilariopsis obliquescostata* indexes, respectively (Gersonde & Zielinski, 2000) and by MAT transfer functions (Crosta, Pichon, & Burckle, 1998a; Crosta et al., 2004). Sea-ice reconstructions were initiated by CLIMAP (1981) and subsequently fell into disuse until the concomitant development of the above-mentioned qualitative and quantitative approaches and performing paleoclimatic models. It was additionally shown that CLIMAP sea-ice estimates in the Nordic seas were spurious (Weilnet et al., 1996), thus creating a resurgence in interest in the LGM period and in Antarctic SIC as important boundary conditions. Records of past SIC focus not only on the LGM (Crosta, Pichon, & Burckle, 1998a, 1998b; Gersonde et al., 2003, 2005), but also on long records (Crosta et al., 2004) and on high-resolution records of rapid climate changes (Hodell et al., 2001; Shemesh et al., 2002; Bianchi & Gersonde, 2002, 2004; Nielsen, Koç, & Crosta, 2004).

The example below represents the only study ever to reconstruct winter and summer sea-ice extents around Antarctica based on the combination of the *Fragilariopsis* proxies and the MAT approach (Gersonde et al., 2005). This comprehensive study conducted on sediments dated from the LGM provides more insight into the seasonal SIC than previous studies (Crosta et al., 1998a; Gersonde & Zielinski, 2000) because of the new modern data set used to estimate sea-ice, the greater area covered, and the comparison of the outputs of both methods whenever possible. SSTs at the LGM were concurrently estimated (Gersonde et al., 2005). It was also the first time that a set of quality controls on the modern data sets, the fossil data sets, and the estimates were provided.

The *F. curta* and *F. obliquecostata* proxies, calibrated by sediment-trap investigations in the South Atlantic (Gersonde and Zielinski, 2000), were applied to 45 LGM samples from the Atlantic and eastern Indian sector of the Southern Ocean (Gersonde et al., 2003). The MAT approach was applied to 73 LGM samples from the Atlantic, Indian, and eastern Pacific sectors of the Southern Ocean (Crosta et al., 1998a). The modern data set was composed of 204 surface sediment samples of recent to subrecent age and involved 31 diatom species. The transfer function is referenced hereafter as $MAT_5204/31$. Modern sea-ice input data were from Schweitzer's (1995) numerical atlas. The $MAT_5204/31$ accurately reconstructed the modern sea-ice distribution of yearly presence and winter concentration/extent with correlation coefficients of 0.97 and 0.96, slopes of the linear regression of 0.96 and 0.93, and mean RMSEP of 0.6 months per year and 6%, respectively. The $MAT_5204/31$ was less efficient in reconstructing the modern sea-ice distribution of summer concentration/extent with a correlation coefficient of 0.8, a slope of 0.6 indicating an overestimation of the estimates, and a mean RMSEP of 4%. Mean root mean square errors of prediction were almost twice as high when samples showing no sea-ice were discarded from the regressions.

The winter sea-ice extent at the LGM, as estimated from diatom assemblages, was 5–10° of latitude of its modern location (Figure 7), thus doubling the winter sea-ice area. This limit, calculated on diatom floral assemblages, is in good agreement with CLIMAP (1981) winter sea-ice limit, which served many years as a reference for paleoclimatic models. Models that compute LGM sea-ice as a consolidated cap calculate a direct effect of Antarctic sea-ice on atmospheric CO_2 concentration of ~70 ppm (Stephens & Keeling, 2000). Models that compute LGM sea-ice as concentration gradients estimated by diatom transfer functions (Crosta et al., 1998b) calculate a pCO_2 drop of 10–30 ppm, thus attributing a lesser direct role to Antarctic sea-ice on atmospheric CO_2 (Morales-Maqueda & Rahmstorf, 2002).

The summer sea-ice extent at the LGM, as estimated from diatom assemblages, was much more extended in the South Atlantic sector of the Southern Ocean, but had a similar extent to today's one in the Indian and eastern Pacific sectors (Figure 7). Although the LGM database does not cover the western Pacific sector, it is believed that LGM summer sea-ice was more extended there relative to the modern cover, as the Ross Sea acts as an ice factory identically to the Weddell Sea. All in all, LGM summer sea-ice cover was obviously greater than the modern one, but diatom-based estimates argue against an area multiplied by 5 as reconstructed by CLIMAP (1981) and Cooke and Hays (1982), who positioned the glacial summer limit around the modern winter sea-ice limit. The new reconstruction implies much less perennial sea-ice cover, which has great implication for the albedo, the CO_2 efflux at the ocean–atmosphere interface, the productivity (Moore, Abbott, Richman, & Nelson, 2000), the hydrological cycle in redistributing salt (Shin, Liu, Otto-Bliesner, Kutzbach, & Vavrus, 2003), and surface water stratification (François et al., 1997). It is absolutely essential to arrive at a more accurate and comprehensive LGM summer sea-ice limit in the near future in order to better constrain paleoclimatic models.

3.3. C, N, and Si Isotopes in the Southern Ocean

The Southern Ocean is one of the largest high-nutrient, low-chlorophyll (HNLC) regions of the world in which low concentrations of trace metals, such as iron, limit productivity (Boyd et al., 2000; Boyd, 2002). Martin (1990) hypothesized that greater iron-bearing dust input during glacial times promoted phytoplanktonic productivity, therefore leading to the recorded reduced glacial atmospheric iron concentrations (Sarmiento & Toggweiler, 1984). However, investigations of deep-sea sedimentary records failed to clearly show the glacial period's increase in productivity, with contradictory results according to the study area and the proxy used (Mortlock et al., 1991; Kumar et al., 1995; Bareille et al., 1998). A decoupling between accumulation rates of organic carbon and biogenic silica has been shown (Anderson et al., 1998). In this context, the question of productivity changes in the Southern Ocean might have been abandoned if the "silicic leakage" hypothesis had not recently been proposed. Laboratory experiments showed that the uptake ratios of N/Si and C/Si by diatoms were greater when iron was not limiting (Hutchins & Bruland, 1998; Takeda, 1998; Brzezinski et al., 2002). *In situ*, it is believed that a

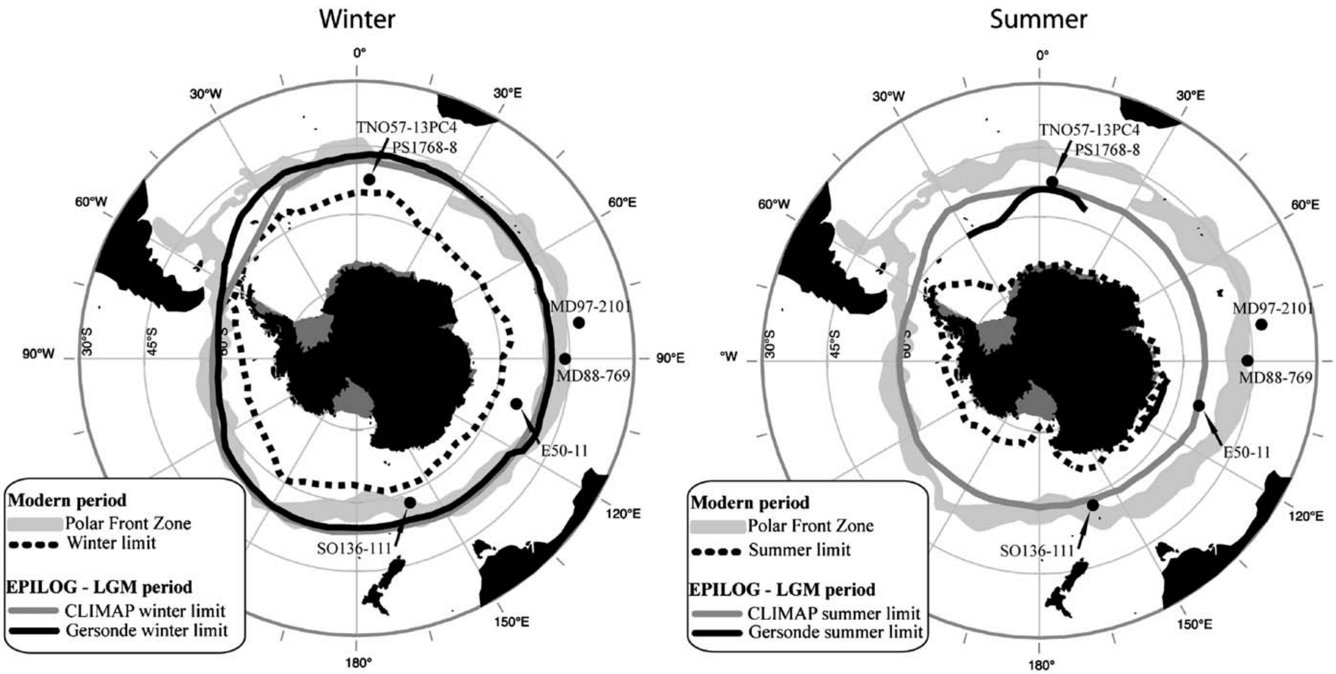


Figure 7 Sea-ice extent at the Last Glacial Maximum during the winter and summer seasons in the context of the MARGO program (modified from Gersonde et al., 2005). Gersonde's winter sea-ice limit was calculated from the *F. curta* group proxy (Gersonde & Zielinski, 2000) and the MAT approach (Crosta et al., 1998a), while Gersonde's summer limit was estimated from the *F. obliquecostata* proxy (Gersonde et al., 2005) and the MAT approach (Crosta et al., 1998a). CLIMAP's winter and summer limits were located at the faunally identified winter and summer 0°C isotherms, respectively (CLIMAP, 1981), and lithogenic tracers such as changes in the sedimentation rate, presence of ice-rafted debris, and geographical contact between diatom oozes and clayey sediments (Cooke & Hays, 1982). Position of the modern sea-ice limits is from Schweitzer (1995), and location of the modern hydrographic fronts is from Orsi, Whitworth, and Nowlin (1995).

higher N/Si uptake ratio during glacial times, stimulated by greater eolian iron input (Petit et al., 1999), led to surface water enrichment in silicic acid. Subantarctic Mode Waters (SAMW) thus supplied more silicic acid to low-latitude phytoplankton, stimulating the growth of siliceous organisms at the expense of carbonate organisms, thus reducing atmospheric CO_2 by decreasing the $CaCO_3/C_{org}$ ratio (Archer, Winguth, Lea, & Mahowaki, 2000). However, little geological evidence supports this hypothesis. In this context, diatom isotopic ratios may provide the best test of the silicic acid hypothesis as they are not affected by remineralization and diagenesis.

DIOM-$\delta^{13}C_{org}$, DIOM-$\delta^{15}N_{org}$, and $\delta^{30}Si$ were analyzed in the same three cores from the Indian sector of the Southern Ocean. Core SO136-111/E50-11 is from the Antarctic Zone, core MD88-769 is from the Subantarctic Zone, and core MD97-2101 is from the southern Subtropical Zone (Figure 7). Stratigraphy of the cores is based on AMS-^{14}C dates subsequently calibrated to calendar ages using CALIB 4.3 software (Stuiver et al., 1998) after removing the reservoir age. In the two southernmost cores, DIOM-$\delta^{15}N_{org}$ and $\delta^{30}Si$ are anticorrelated while DIOM-$\delta^{13}C_{org}$ and $\delta^{30}Si$ are positively correlated (Figure 8, APF and SAF boxes). Discarding potential modification of the nitrate to silicic acid supply ratio by the upwelling of Circumpolar Deep Water, anticorrelated DIOM-$\delta^{15}N_{org}$ and $\delta^{30}Si$ records argues for different relative uptake of nitrate and silicic acid through time, with greater uptake of nitrate during the last glacial and greater uptake of silicic acid during the Holocene. These changes are in agreement with the dust concentration record of Vostok (Petit et al., 1999), indicating a potential role of iron deficiency alleviation on diatom physiology during glacial times (Crosta et al., 2005b; Robinson et al., 2005; Beucher et al., 2006). The remnant nutrient pool in Antarctic surface waters was therefore enriched in nitrate during the Holocene and enriched in silicic acid during the last glacial period. Antarctic surface waters circulate around Antarctica within the Antarctic Circumpolar Current but have a northward component due to the Coriolis force and cross-frontal eddy diffusion. One should expect similarly anticorrelated Si and N isotopic signals in the northernmost core located on the Southern Subtropical Front if Antarctic Surface Waters were advected as far north. Nitrogen and silicon isotopic records in core MD97-2101 are, however, correlated (Figure 8, SSTF box). This indicates that N/Si uptake ratios by diatoms remained almost constant over the last 50,000 yr, which has two implications. First, no iron supply modified diatom physiology in the northern part of the Indian sector of the Southern Ocean, in agreement with the reconstruction of dust deposition at the LGM (Andersen, Armengaud, & Genthon, 1998). Second, no Antarctic surface waters reached the latitude of the core location, but they were seemingly transformed in SAMW that fueled low-latitude upwelling systems with waters enriched in silicic acids (Crosta et al., 2005b; Beucher et al., 2006). Investigations of diatom isotopic ratios thus provide support to the silicic acid hypothesis, although it is still impossible to quantify the amplitude of N/Si changes in the SAMW, and therefore the real impact on atmospheric CO_2 concentrations (Matsumoto, Sarmiento, & Brzezinski, 2002). Investigations of diatom isotopic ratios in low-latitude upwelling systems may help in resolving this issue.

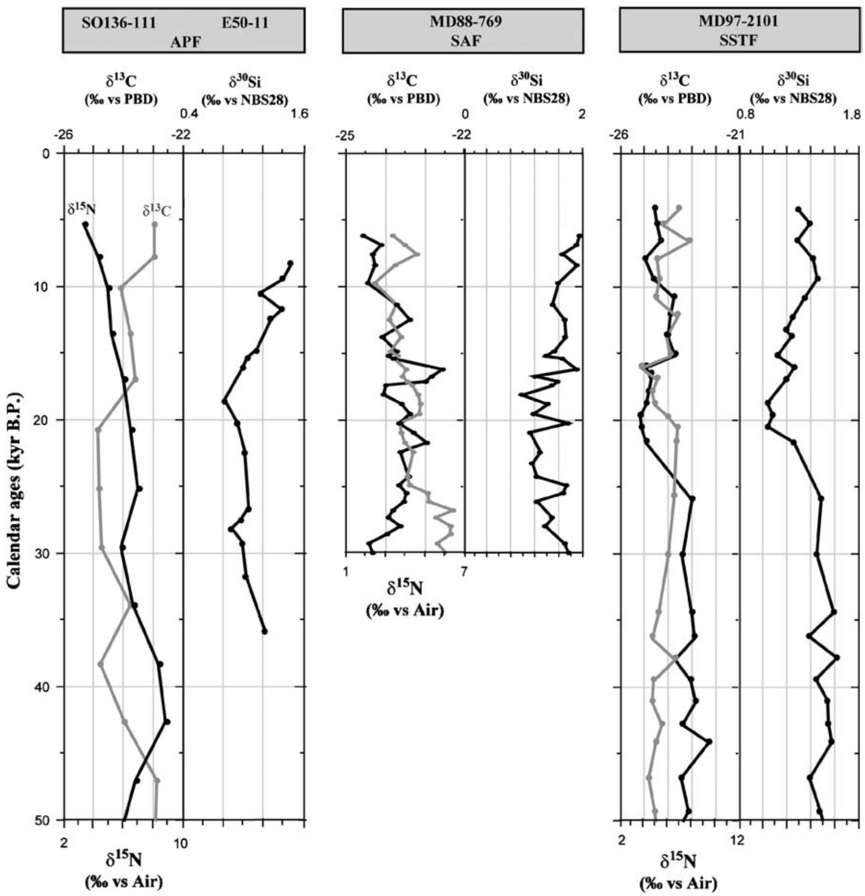


Figure 8 Carbon, nitrogen, and silicon isotopes in diatoms versus age from the Antarctic Polar Front Zone (APF), the Subantarctic Front (SAF), and the Southern Subtropical Front (SSTF) (De La Rocha et al., 1998; Crosta et al., 2005b; Beucher et al., 2006). Positions of the cores are shown in Figure 7.

As illustrated above, several methods using diatoms have been developed during the last couple of decades, providing scientists with exceptional tools to reconstruct past ocean conditions. There is no doubt that further application of these methods to high-latitude, upwelling and coastal regions of the world's oceans will enhance our understanding of climate change at all time scales.

4. CONCLUSION

Due to their distribution from oceanic to fresh waters and their ability to synthesize a siliceous test that is generally well preserved in the sediments, diatoms have received a great amount of attention. Thanks to the constant advancement of the analytical techniques, the improving understanding of the ecology and physiology of diatoms, and the drilling of better/longer sedimentary deep-sea cores, diatoms are now used to investigate past changes of a wide range of oceanographic parameters. Reconstruction of SSTs, sea-ice cover, water mass fluxes, fresh water input, productivity, and nutrient cycling represent only a small part of what it is potentially possible to do using diatoms, in both the fields of micropaleontogy and sediment geochemistry. These same parameters are also the most important in paleoclimate modeling, and can be used as boundary conditions or as an independent external check of model output. Paleoclimatic models are generally coupled with thermodynamic sea-ice models that, although fully interactive, may not provide accurate seasonal sea-ice extent and concentration. In this context, extensive reconstructions of sea-ice cover at key periods and at Milankovitch scale are greatly needed. Diatoms are the main tool to achieve quantitative estimates of Antarctic sea-ice extent and concentration, although chemical content of ice cores may provide complementary information (Wolff et al., 2006).

Future developments of the diatom methods will mainly concern geochemistry. Currently, a great effort is being made to obtain reliable radiocarbon dates from the organic compounds intrinsic to diatom frustules (Ingalls, Anderson, & Pearson, 2004), in order to help in dating sediments devoid of foraminifera, to measure silicon isotopes (Beucher et al., 2006) and oxygen isotopes (Swann, Maslin, Leng, Sloane, & Haug, 2006), to quantify production and dissolution of diatoms (Nelson, Tréguer, Brzezinski, Leynaert, & Quéguiner, 1995; Tréguer et al., 1995), and to understand biomineralization of the frustule (Martin-Jézéquel, Hildebrand, & Brzezinski, 2000) in order to help reconstruct modern and past silica cycles.

However, developments regarding micropaleontology should not be ignored. Slide preparation and diatom census counts are very long processes that would greatly benefit from automatic microfossil recognition. Although we know that diatom intra-specific variability is high, and that specimens may be present in different states of preservation, or even be tilted on the permanent slide, it might be possible in the future to have access to the most prominent species or group of species with acceptable taxonomic precision. Laminated sediments were recently discovered in different oceanic regions and can be used to reconstruct climate changes at a seasonal scale over the whole Holocene period. Two aspects, nevertheless, have to be addressed. First, modern diatom ecology needs to be better understood at the seasonal scale in the regions where such exceptional records exist: the coastal Antarctic (Leventer, Domack, Barkoukis, McAndrews, & Murray, 2002; Maddison et al., 2005; Stickley et al., 2005; Denis et al., 2006), Baja California (Pike & Kemp, 1999; Kemp et al., 2000), fjords along the Canadian West Coast (Hay et al., 2003), and the Red Sea (Seeberg-Elverfeldt, Lange, Arz, Pätzold, & Pike, 2004). Sediment-trap investigations along the Canadian West Coast have already begun to provide more insights into diatom seasonal succession and ecology (Hay et al., 2003; Dallimore et al., 2005). Second, techniques to accurately determine diatom species and sediment composition on thin sections need to be further developed (Pike & Kemp, 1996; Pike, Bernhard, Moreton, & Butler, 2001; Denis et al., 2006).

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